

into a water-based medium, or a method for the preparation of urethane-urea/ethylenic resin composite type crosslinked particles obtained by polymerizing a polymerizable ethylenic unsaturated compound containing at least the hydroxyalkyl (meth)acrylate composition modified by a small amount of lactones in water in which crosslinked urethane-urea particles are dispersed, and, in addition, intends to provide a coating which comprises containing thus-obtained various crosslinked particles as essential thin layer-formable resin components.

Herein, specified crosslinked particles to be employed in the present invention are obtained by dispersing and crosslinking a mixture of the acrylic polyol resin (VI-A) having carboxylic groups and crosslinkable functional groups with the polyisocyanate compounds (VI-B) (a hydrophobic crosslinking agent) into a water-based medium.

That is, the acrylic polyol resin (VI-A) to be employed for the preparation of the specified crosslinked particles is a so-called self water-dispersible resin which simultaneously contains carboxylic groups which are a hydrophilic segment and crosslinkable functional groups which can react with the polyisocyanate compounds (VI-B) (a hydrophobic crosslinking agent), and which means a resin which forms an O/W discontinuous phase by emulsifying through a phase inversion while adding water into an organic continuous phase (O).

In the case, it is a resin which is basically different from a water-soluble resin. Further, such the self water-dispersible resin is accompanied by a physical and chemical phenomenon of a phase inversion from organic phase to water phase, and it has an ability of forming O/W particles in a water-based medium. In the case, hydrophobic

substances can be taken into particles.

The present invention intends to provide highly-crosslinked particles which have not been conventionally prepared by emulsifying the polyisocyanate compounds (VI-B) (a hydrophobic crosslinking agent) together with the self water-dispersible resin into a water-based medium through a phase inversion utilizing characteristics of such the self water-dispersible resin to take the polyisocyanate compounds (VI-B) into the particles, and then, by proceeding a crosslinking reaction.

Further, a coating which contains such the crosslinked particles as an essential component can provide a coating layer having a very excellent corrosion resistance.

If the acrylic polyol resin (VI-A) is a water-soluble resin, since particles are formed by the hydrophobic crosslinking agent which functions as a nucleus, stability becomes insufficient in the water-based medium, and it is apt to be readily gelled during proceeding the crosslinking reaction, or it tends to gel with a lapse of time.

The crosslinked particles obtained by a method for the preparation in the present invention are mixed with the acrylic polyol resin (VI-A) and the polyisocyanate compounds (VI-B) (a hydrophobic crosslinking agent), followed by dispersing into a water-based medium by adding a basic material.

As the basic material to be employed herein, volatile tertiary amines are preferably employed and, contrarily, inorganic basic compounds unpreferably remain in a coating layer, and show a tendency that water resistance becomes worse.

As the amines, there are exemplified particularly typical examples

alone, and there are enumerated a variety of alkyl amines such as trimethylamine or triethylamine; a variety of alcohol amines such as dimethylaminoethanol, diethanolamine or aminomethylpropanol; and a variety of cyclic amines such as morpholine.

Subsequently, after dispersing into a water-based medium, solvents are optionally removed and, in the case that the polyisocyanate compounds are contained, heating is conducted at 50-60°C for 1 hour or so, and, in the case that an epoxy resin is contained, heating is conducted at 80°C or so for 1-2 hours or so to accelerate a crosslinking, and then, there can be obtained a water dispersion liquid containing crosslinked particles having a desired solid content by removing water.

Further, in the present invention, there can be employed the following type ones as a urethane/acrylic resin composite type crosslinked particles. That is, the type ones are obtained by 1) first of all, a water dispersion containing crosslinked urethane particles are independently prepared, subsequently, 2) a low polymerizable vinyl-based monomer in relation to the present invention is added dropwise into the water dispersion under the presence of a radical polymerization initiator (it is a so-called seed polymerization method) to effect polymerization.

Herein, as a method for obtaining a water dispersion of crosslinked urethane particles, three methods are outlined. Since all methods are a publicly-known method to a skilled person in the art, outlines alone are illustrated. First of those is a method in which there is emulsified a polyisocyanate prepolymer having isocyanate groups at terminals in the molecule under the presence of an emulsifier and/or a water-soluble resin for a protecting colloid, and then, the isocyanate groups at

terminals are crosslinked by adding a crosslinking agent such as polyamines to obtain desired crosslinked particles.

Second of those is a method in which any one of anionic, cationic, and nonionic hydrophilic groups is introduced as pendant groups into a molecule of the polyisocyanate-prepolymer having an isocyanate groups at terminals, whereby, the prepolymer itself is self-emulsified without using an auxiliary agent such as an emulsifier and, polyamines which are a crosslinking agent are likewise added to prepare crosslinked particles.

Third of those is a method in which the same prepolymer as in the second method is mixed with the hydrophobic polyisocyanate compounds, and then, emulsified by a phase inversion into a water-based medium, and a polyamine which is a crosslinking agent is added after introducing the hydrophobic polyisocyanate compounds into particles to prepare crosslinked particles.

Of those, in the second and third methods, although auxiliary agents may be even simultaneously employed, it is preferred to not simultaneously employ the auxiliary agents in consideration of succeeding steps.

For that reason, in the present invention, it is required that it is often desired to employ crosslinked urethane particles obtained by the second and third methods in which the auxiliary agents such as emulsifiers are not simultaneously employed.

In a polymerization step of a polymerizable vinyl-based monomer typified by the hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones in relation to the present invention by

employing the crosslinked urethane particles dispersion as a seed, a characteristic part is to employ a crosslinked urethane water dispersion as a seed material and, needless to say, as a method for the polymerization of the vinyl-based monomer, conventional methods can be employed without any modification.

As the radical polymerization initiators, any one of water-soluble or oil-soluble ones can be employed and, above all, water-soluble radical initiators can be more readily employed, and those can also contribute to a dispersion stability in the water dispersion of a composite resin obtained, accordingly, those are more desired.

As weight ratio of solid components in the crosslinked urethane resin (GU) with respect to the polymerizable vinyl-based monomer (VM), although there can be applied a range of $0/100 < \text{GU}/\text{VM} < 100/0$, in the case that there are not employed auxiliary agents such as emulsifiers at all, it appropriately ranges in $20/80 < \text{GU}/\text{VM} < 100/0$ depending upon a gel density (a crosslinking density) and dispersion stability of a gel-urethane to be employed.

However, since a main purpose of modification for a composite is to allow to manifest all properties of both the above-described crosslinked urethane resin (GU) and a polymer derived from the polymerizable vinyl-based monomer (VM), in order to allow to manifest all the properties of both resins, it ranges in $10/90 < \text{GU}/\text{VM} < 90/10$, and preferably in $25/75 < \text{GU}/\text{VM} < 75/25$, and the range is particularly recommended.

The polymerizable vinyl-based monomers may be even added dropwise to a seed system maintained under conditions of reaction temperatures or, may be even added dropwise to a seed system maintained under

conditions of reaction temperatures after having absorbed the polymerizable vinyl-based monomers in swelled seed particles under conditions of reaction temperatures.

Such the dropwise addition is mainly conducted for the purpose of controlling a reaction heat accompanied by polymerization, accordingly, a method for the dropwise addition is not particularly limited.

In thus-obtained composite type water dispersion of a crosslinked urethane resin/vinyl-based resin, in the case of employing a multifunctional vinyl-based monomer, networks derived from both resins are intertwined each other and the so-called IPN is formed and, as a result, there can be obtained a product having more excellent solvent resistance and chemical resistance, and a high tensile force.

Incidentally, in a method of the present invention, there can be formed a coating layer which is particularly excellent in corrosion resistance from a coating containing crosslinked particles having characteristics as described hereinabove as an essential thin layer-formable resin component, accordingly, the present inventor names the method as a gel particle layer-forming method.

That is, the present invention intends to provide a method for the formation of a coating layer having a corrosion resistance for a metal, namely, the gel particle layer-forming method in which there is employed a coating agent containing more than 50% by weight of the above-described crosslinked particles having a particle diameter of not more than 1 micron (μm) as an essential thin layer-formable resin component in the case of the formation of a coating thin layer having

corrosion resistance for a metal or a decorative coating layer having corrosion resistance for a metal by coating a liquid coating agent (a liquid coating) onto a metal to be coated and drying and, by heating at a temperature of 100-350°C or so for a fixed time of period.

After all, there was found that in the gel particle layer-forming method, crosslinked particles themselves are crosslinked each other according to a design level of the crosslinked particles, whereby, a continuous thin layer can be formed, or a continuous thin layer can be formed through a crosslinking between a particle and a particle by employing together a crosslinking agent and, further, the method does not cause any inconveniences and, as a result, any problems even though there is employed together a melamine resin-based curing agent having a problem in a conventional method for forming a layer as a crosslinking agent, and the present invention has been completed.

In other words, a following mechanism is guessed, that is, the crosslinked particles are formed by strong bonds against a variety of chemicals such as acids and alkalis and, in addition, a main component for a thin layer-formable resin is constructed by the crosslinked particles crosslinked in a level of not being apt to swell in solvents, whereby, even though crosslinked bonds between particles are a so-called weak bond against chemicals such as methylene ether bond which is produced in the case of employing the melamine resin-based curing agent, since the bond is protected from every direction by the crosslinked particles, those become not apt to be directly attacked by chemicals, as a result therefrom, there manifests an excellent effect that it is suppressed to cause a problem such as decomposition.

In addition, the crosslinked particles are a peculiar one molecule

compound having a gelled (cross-linked) giant molecular weight. If roughly estimated, a molecular weight in a one molecule compound particle having a size of $1\mu\text{m}$ will attain to at least 300,000,000.

Needless to say, a thin layer-formable resin to be employed in a form of a conventional coating is of a level of a so-called prepolymer, and the molecular weight is 100000 or so to the utmost.

In the gel layer-formable method in the present invention which starts from the crosslinked particles having a giant molecular weight, a continuous crosslinked gel layer is formed by production amount of chemical binds which are exceedingly slight compared to production amount of chemical binds to be required for preparing a crosslinked gel film having a sufficiently high molecular weight by forming a coating layer through crosslinking thereof, that is, by production amount of 1 piece per 0.3 billion pieces, whereby, a molecular weight in a coating layer produced can attain to an extraordinary level.

In other words, in such the gel particles layer-formable method which starts from a giant molecule, the production amount of chemical binds to be required in layer-forming may be even substantially very slight compared to conventional methods.

This means that temperature, time of period, or an amount of a catalyst which is a condition to be required for producing a chemical bond can be all reduced or shortened and, particularly, in the case that a cross-linking agent is simultaneously employed, use amount thereof can be more reduced.

This is also a large characteristics in the present invention.

In construction of the above-described liquid coating agent (a liquid coating) in the present invention, more than 50% by weight of

the cross-linked particles are desirably contained as a resin component for film-forming (a thin layer-formable resin component).

Even in the case of being less than 50% by weight, although an only about effect is shown, it is not sufficient. Preferably, it is not less than 70% by weight.

In order to obtain a glossy coating surface having smoothness, it may safely be said that there is required a particle diameter of not more than 1 μ m by all means and, moreover, a smaller diameter is more preferred. Further, it is desired to contain a component having a specified chemical bond such as urethane bond, whereby, a coating layer obtained becomes hard, flexible, and tough.

By giving a so-called active atomic group (a polar group) such as hydroxyl group, carboxylic group, glycidyl group, or urethane bond into the particles, gel particles themselves are self crosslinked, or by crosslinking between particles in the form of employing together with a curing agent (a cross-linking agent), a continuous thin layer can be formed herein.

Such the crosslinking reaction is usually induced by forcibly heating, and completed.

Although depending upon a kind of a reactive active group (a reactive polar group), in order to complete the reaction within an appropriate time of period, there is by all means required a temperature of not less than 100°C, and preferably not less than 120°C.

If the reactive active group (a reactive polar group) is a variety of unsaturated bonds such as vinyl group, since crosslinking is caused even by irradiation of so-called radiation rays such as an ultraviolet ray and an electron beam, although it does not always require to be

heated, heating is also preferably conducted in order to proceed a reaction by accelerating a close fusion of particles themselves.

In the case that the curing agent is simultaneously employed, as such the curing agent, there can be employed a variety of compounds such as a melamine resin, a phenol resin, and an isocyanate compound and, in order to obtain a coating layer having a light color by exposure and heating, the melamine resin is preferably employed.

For example, in a water-based coating, a water-soluble or water-dispersible melamine resin is exemplified, and particularly typical examples alone are exemplified below, which include a hexamethoxymethyl melamine such as "MW12LF" manufactured by Sanwa Chemical, Ltd., "Nikalak MW-30" manufactured by Nihon Carbide Kagaku Kogyo, Ltd., or "Sumimal M-100C" manufactured by Sumitomo Kagaku Kogyo, Ltd., and a variety of methoxymethyl melamines which have free methylol group such as "Sumimal M-40W" and "Sumimal M-30W" manufactured by Sumitomo Kagaku Kogyo, Ltd.

Further, there can be also employed a melamine resin in which a so-called hydrophobic melamine resin diluted in a dilution ratio of not more than 20% by weight using water/methanol mixed solvent (weight ratio=35/65) is dispersed by a water-soluble resin or a dispersant and, above all, the hexamethoxy melamine resin is employed.

And, use amount of the curing agent appropriately ranges in 1-25% by weight, and preferably 3-15% by weight based on amount of the crosslinked particles. As a thin layer-formable resin component other than the curing agent typified by the crosslinked particles and the above-described melamine resin, there can be also simultaneously employed a thermoplastic resin having a reactive active group (a

reactive polar group), and use amount of the thermoplastic resin having a reactive active group appropriately ranges in not more than 30% by weight, and preferably not more than 20% by weight in the thin layer-formable resin component.

When there more increases the use amount of components other than the curing agent, various inherent properties in the gel layer-forming method are more deteriorated and, there becomes also more deteriorated an effect for manifesting a high corrosion resistance which is a target property.

Further, if an average molecular weight between crosslinking points in the above-described various crosslinked particles ranges in 300-2,000, in the coating of the present invention essentially containing the crosslinked particles, corrosion resistance becomes more preferred.

Incidentally, the average molecular weight between crosslinking points described herein is shown by a weighted average value after having calculated an average molecular weight per 1 piece of a functional group taking part in crosslinking in respective resins (also including the hydrophobic curing agent) to be formulated.

It is to be noted that a temperature for film-forming in the crosslinked particles is preferred in not more than 100°C.

In the case of crosslinked particles which do not form a thin layer without heating at a temperature of more than 100°C even though a variety of solvents are employed as an auxiliary agent for film-forming, the temperature for film-forming should be designed so as to become not more than 100°C because of a difficulty in obtaining a coating layer which is excellent in corrosion resistance which is one of purposes

in the present invention and, also from a viewpoint of formulating composition or a crosslinking density.

Further, in the case that the average molecular weight between crosslinking points is less than 300, that is, in the case that the crosslinking density is exceedingly high, as a result, it affects to the temperature for film-forming, fusion between particles or film-formation (thin layer-formation) become difficult, and various properties as a coating layer are unpreferably deteriorated.

On the other hand, in the case that the average molecular weight between crosslinking points becomes too large exceeding 3,000, that is, in the case that the crosslinking density is low, as a result, the particles become apt to swell in a solvent, resulting in that solvent resistance also unpreferably lowers.

In the coating of the present invention, needless to say, pigments can be also involved in the crosslinked particles which are an essential component in the coating. By involving the pigments in the crosslinked particles, the present invention has a merit of liberation from various problems by removing all drawbacks such as dispersibility and color-separation of pigments which have still become problematic until now.

Particularly, in a water-based coating, since a excellent dispersant does not exist and, pigments are mainly dispersed using a water-soluble resin and, there is applied a method that the pigments are added and involved. On the other hand, in the present invention, pigments can be optionally involved without any modification in the crosslinked particles and, whereby, there can be removed an influence which depends upon surface conditions of a variety of pigments. Moreover,

since the pigments are covered by particles having a crosslinked structure, particles are not swelled or not dissolved by solvents contained in a composition, whereby, there is also produced a merit that pigments are not separated and an excellent dispersibility and stability are shown.

Specifically, the above-described acrylic polyol resin (VI-A) (a self water-dispersible resin) and the pigments are kneaded by a publicly-known and common method, for example, using a variety of apparatuses such as a three-roll and a paint conditioner to prepare a mill base, subsequently, the above-described polyisocyanate compound (VI-B) (a hydrophobic crosslinking agent) is mixed therewith and amines are added, followed by dispersing into an aqueous medium.

After that, there is obtained a desired water dispersion in which pigments are involved in crosslinked particles by accelerating crosslinking. Roughly, there is obtained a desired water dispersion in which pigments are involved through the means and steps as described hereinabove.

Such the methods are particularly effective in the case of producing particles by emulsifying through a phase inversion using the self water-dispersible resin. It is very difficult to prepare a such capsule of pigments by a publicly-known and common means, for example, a method such as an emulsion polymerization or a nonaqueous polymerization (a nonaqueous-dispersion polymerization).

Herein, particularly typical examples alone are enumerated as pigments to be employed, and there are enumerated a variety of inorganic-based pigments such as titanium dioxide (for example, Typek CR-95 (a titanium oxide pigment manufactured by Ciba Geigy, A.G.)),

an iron oxide, an iron oxide red, lead molybdenum, chromium oxide, and a chromate or carbon black; or a variety of organic-based pigments such as a phthalocyanine-based pigment such as Phthalocyanine Blue and Phthalocyanine Green, Carbazole Violet, Anthrapyrimidine Yellow, Flavaslone Yellow, Isoindoline Yellow, Indaslone Blue or Quinaklidone Violet, Quinaklidone-based Red, an azo pigment, and an anthraquinone pigment, etc.

Further, although the crosslinked particles as described hereinabove are a water-based one, the crosslinked particles employed in the present invention can be employed in a wider composition range compared to so-called nonaqueous crosslinked particles obtained by a method such as the nonaqueous polymerization (a nonaqueous-dispersion polymerization) and, moreover, a preparation process is also easy.

The crosslinked particles in the present invention can be readily moved into a variety of polar organic solvents such as, for example, butanol and methylethylketone. In the case, it can be returned from carboxylic salts to carboxylic acids by a reverse neutralization and, whereby, it can be readily further moved.

As described hereinabove, in the present invention, water-based crosslinked particles can also become employed in a solvent system. However, although being a little, since it tends to become slightly poor in dispersion stability compared to a water-based one, it may safely be said even that it rather matches with a water-based use in the method for the preparation of the crosslinked particles of the present invention and a coating obtained using the crosslinked particles.

The coating in relation to the present invention essentially contains the above-described curable resin composition, and the coating is obtained by dissolving or dispersing the resin into water and, there can be prepared a two-liquid coating composition or a single-liquid coating composition by optionally formulating a variety of additives which are conventionally employed in a coating field, for example, an ultraviolet ray absorbent, a photostabilizer, an antioxidant, a coloring pigment, an extender pigment, a metallic pigment, an aluminum powder, a pearly mica powder, an anti-dropping agent or an anti-sedimentation agent, a leveling agent, a dispersant, a defoaming agent, an antistatic agent, a catalyst for curing, a flowability-adjusting agent, a cellulose acetate-butylate, and a thinner which are publicly- and commonly-known. Further, there can be employed other resins such as an epoxy resin and a polyester resin or a high molecular weight compound which has a good compatibility within a range in which an effect by the present invention is not decreased.

Thus-obtained coating can be coated by publicly- and commonly-known methods such as spray coating, roller coating, and brush coating. It is to be noted that it goes without saying that the resin composition for a coating of the present invention can be employed as a clear coating in which pigments are not employed, or an enamel coating in which pigments are employed.

In the coating in relation to the present invention, there can be actualized a more exceedingly excellent acid resistance which does not include any problems compared to a coating prepared from a

conventional polyol and melamine resin even though being further simultaneously employed other polyols and crosslinking agents (for example, a melamine resin). In the coating in relation to the present invention, in the case of simultaneously employing other polyol resins and melamine resins, the content of the curable resin composition of the present invention is not less than 10% by weight, and preferably not less than 25% by weight, the melamine resins are not more than 30% by weight, and preferably not less more than 20% by weight, in total solid resin components.

In the case that the curable resin composition of the present invention is less than 10% by weight or, the melamine resins are more than 30% by weight, an acid resistance cannot be unpreferably elevated.

In the curable resin composition of the present invention, above all, in order to elevate weatherability such as retention of a gloss during exposure and a high extentionable property, there is preferably employed a mixture composed of an ultraviolet ray absorbent/hindered amine-based photo-stabilizer=(40-60)/(60-40) (solid content ratio) within a range of 0-10 wt% based on solid components in the curable oligomer (a (co)polymer) (a). In the case that addition amount is not less than 10 wt%, since a price of a coating becomes expensive and, crystallines are occasionally formed at a low temperature and water resistance occasionally lowers, and a resin solution occasionally discolors, it is not preferred so much. Even in an outside value of the above mixing ratio of the ultraviolet ray absorbent with respect to the hindered amine-based photo-stabilizer, although an effectiveness is observed, the effectiveness is excellently observed in a range of the above mixing ratio.

As typical examples of the ultraviolet ray absorbent which is publicly-known, there can be preferably employed a benzotriazole-based ultraviolet ray absorbent such as Tinuvin 900, Tinuvin 383, and Tinuvin P (all of those are manufactured by Ciba Geigy), an anilide oxalate-based ultraviolet ray absorbent such as Sandbar 3206 (manufactured by Sand), etc. A fixed amount of the absorbents may be added in a terminating period of a copolymerization reaction of the acrylic polyol or in the preparation of a coating. On the other hand, in the case of T-17, T-37, and T-38 (all of those are a product by Adeka Argus Kagaku, Ltd.) which are a reactive ultraviolet ray absorbent containing an organic group having an ultraviolet ray absorbing ability such as an O-hydroxybenzophenone group and an ethylenic copolymerizable unsaturated bond such as methacrylic acid group in an identical molecule, a fixed amount thereof may be simultaneously introduced at a copolymerization step of the acrylic polyol resin (VI-A) components.

As examples of the hindered amine-based photo-stabilizer, there can be preferably employed a piperidine-based one which is usually called HALS (HALS), and which typically includes 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, bis(2,2,6,6-tetramethyl-4-piperidine)sebacate, or Tinuvin 144, 292, and 765 (all of those are a product manufactured by Ciba Geigy, A.G.), MARK LA-57, 62, 63, 67, and 68 (all of those are a product by Adeka Argus Kagaku, Ltd.), Sanol LS292 (manufactured by Sankyo), and Sandbar 3058 (manufactured by Sand). A fixed amount of the stabilizers may be added in a terminating period of a copolymerization reaction of the curable oligomer (a (co)polymer) (a) or in the preparation of a coating. In the case of a hindered amine-based compound containing

an organic group having a photo-stabilizing ability and an ethylenic copolymerizable unsaturated bond such as (meth)acrylic acid group such as the MARK LA-82, 87, and T-41 (all of those are a product by Adeka Argus Kagaku, Ltd.), a fixed amount thereof may be simultaneously introduced at a synthesis step of the curable oligomer (a (co)polymer) (a).

Further, in order to increase an effectiveness thereof, optionally, there can be simultaneously employed an antioxidant such as "Sumilizer BHT" (a product manufactured by Sumitomo Kagaku Kogyo, Ltd.), "Seenox BCS" (a product manufactured by Shiroishi Calcium, Ltd.), "Irganox 1010 or 1076" (a product manufactured by Ciba Geigy, A.G.), "Noclizer TNP" (a product manufactured by Ohuchi Shinko, Ltd.), and "Antioxidant KB" (a product manufactured by West Germany/Bayer. A.G.), which are well known and commonly-used.

As the catalysts for curing, there are enumerated a phosphate, an organic acid such as dodecylbenzene sulphonic acid or paratoluene sulphonic acid and an amine salt thereof, an organic tin compound such as dibutyltin dilaurate and dibutyltin dimaleate and a chelating compound thereof, etc.

As the extender pigment, for example, there are enumerated kaoline, talc, silica, mica, barium sulphate, and calcium carbonate, etc.

As the anti-dropping agent or an anti-sedimentation agent, for example, there can be preferably employed bentonite, a castor oil wax, an amide wax, a microgel (for example, MG100S (manufactured by Dainippon Ink)), and aluminum acetate, etc.

As the levelling agent, for example, there can be preferably employed a silicone-based surface active agent such as KF69, Kp321

and Kp301 (manufactured by Shin-etsu Kagaku), a silicone-based surface active agent such as Modaflow (a surface-adjusting agent manufactured by Mitsubishi Monsanto) and BYK301 and 358 (manufactured by Bickchemie Japan), and Diaaid AD9001 (manufactured by Mitsubishi Rayon), etc.

As the dispersant, for example, there can be preferably employed Anti-Terra U or Anti-Terra P, and Disperbyk-101 (manufactured by Bickchemie Japan), etc. As the defoaming agent, for example, there can be preferably employed BYK-0 (manufactured by Bickchemie Japan), etc.

As the thinner, there can be preferably employed conventionally publicly-known aromatic compounds, alcohols, ketones, ester compounds, or a mixture thereof, etc.

As the antistatic agent, for example, there can be preferably employed Esocard C25 (manufactured by Lion Armer), etc.

In the case of preparing the coating composition of the present invention, there are mixed the above-described acrylic polyol resin (VI-A), the polyisocyanate compound (VI-B), and optionally, additives such as curing agents and pigments, and uniformly dispersed by a dispersing machine such as a sand grind mill, a ball mill, and Atlighter to prepare a curable type coating composition.

A method for coating the curable coating composition (a coating composition) of the present invention is as follows.

That is, an article to be coated is cleaned by a publicly-known dewaxing cleaning, for example, dewaxing by an organic solvent such as 1,1,1-trichloroethane, cleaning by an alkali, cleaning by an acid,

wiping by a solvent, etc., further, optionally, in order to further elevate an adhesive power of a coating to the article to be coated, for example, the coating composition of the present invention is directly coated by an air-spraying coating method and an airless coating method after coating a primer such as Primac NO. 1500 (manufactured by Nihon Yushi), and optionally, it is set for 0.5-120 minutes, and preferably 1-20 minutes, and thermally cured (baked) at a low temperature of 90-140°C, and preferably 100-120°C. A clear coating may be even coated onto a base coat coating which is an under layer by a wet-on-wet method. In the present invention, since curing can be conducted at a low temperature of not more than 140°C by the above-described construction, it does not give a damage even on a polyolefine-based resin molded article, and there can be formed a coating layer having excellent properties of a coating layer.

In the case that a primer is coated, layer thickness after drying is generally 3-20 μm , and preferably 5-15 μm . Further, layer thickness of the clear coat coating is generally 15-45 μm , and preferably 20-35 μm . As a method using the coating composition of the present invention, there are enumerated a 2-coat/1-baking type coating method and 3-coat/2-baking type coating method, etc.

Herein, the 2-coat/1-baking type method is one of coating methods by an over coating and, first of all, there is coated a base coat coating in which pigments and/or metal powder are formulated in a large amount, and then, there is coated a transparent clear coating or a top coating which is a color clear coating containing a small amount of pigments, and those coatings are simultaneously baked. In the case of the

2-coat/1-baking type coating method, a usual coating composition is employed as a base coat and, the coating composition of the present invention can be employed as a top coat. In the case of the 3-coat/2-baking type coating method, there is coated and baked a coating in which there are formulated pigments, dyes, and/or metal powder and, there is further coated thereon and baked a base coat in which there are formulated pigments, dyes, and/or metal powder, and then, there is coated thereon and collectively baked a transparent clear coating or a top coat which is a color clear coating containing a small amount of pigments or dyes.

VII.

Hereinafter, the present invention VII is illustrated in detail.

(A) Acrylic resin

Acrylic polyol resin (VII-A) (also called the component (VII-A)) is an acrylic resin having hydroxyl group composed of the hydroxyalkyl (meth)acrylate composition (a) modified by a small amount of lactones illustrated in the present invention I.

By polymerizing the hydroxyalkyl (meth)acrylate composition (a) modified by a small amount of lactones employed in the present invention, a main chain is substantially composed of an acrylic copolymer chain, whereby, there are improved weatherability, solvent resistance, and water resistance in a cured article.

In the acrylic polyol resin (VII-A), a molecular weight and a hydroxyl value, etc. are not particularly limited, and a number molecular weight is preferably 1,000-50,000, and more preferably 2,000-30,000 from a viewpoint of physical properties in a coating layer

such as strength and durability. Further, the hydroxyl value is 10-300 mg-KOH/g, and more preferably 30-150 mg-KOH/g from a viewpoint of physical properties in a coating layer such as strength and durability. Such the component (a) may be employed solely or in combination of two or more kinds.

The acrylic polyol resin (VII-A), in addition to the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactones, can be obtained, for example, by copolymerization of other vinyl monomers having hydroxyl group with monomers for introducing a functional group which is illustrated hereinafter, and a (meth)acrylic acid derivative, etc.

Other vinyl monomers having hydroxyl group

As specific examples of the other vinyl monomers having hydroxyl group contained as a copolymerizing component in the acrylic polyol resin (VII-A), there are enumerated the monomers exemplified in the present invention I.

For introducing acid anhydride groups into the acrylic polyol resin (VII-A), for example, maleic anhydride and itaconic anhydride, etc. are copolymerized and, for introducing epoxy groups, for example, glycidyl(meth)acrylate, etc. are copolymerized, and for introducing carboxylic groups, for example, there are copolymerized unsaturated carboxylic acids such as (meth)acrylic acid, maleic acid, fumaric acid, and itaconic acid, etc. and, for introducing amino groups, for example, there are copolymerized vinyl-based monomers containing an amino group selected from the group consisting of primary amino group, secondary amino group, and tertiary amino group.

As a typical example of the vinyl-based monomers containing an amino group, there are enumerated the vinyl-based monomers exemplified in the present invention I.

Derivatives of acrylic acid or methacrylic acid copolymerizable with the other vinyl monomers having hydroxyl group are not particularly limited and, as specific examples, there are enumerated methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, stearyl(meth)acrylate, benzyl(meth)acrylate, cyclohexyl(meth)acrylate, trifluoroethyl(meth)acrylate, pentafluoropropyl(meth)acrylate, perfluorocyclohexyl(meth)acrylate, (meth)acrylonitrile, (meth)acrylic amide, α -ethyl(meth)acrylic amide, N-butoxymethyl(meth)acrylic amide, N,N-dimethyl acrylic amide, N-methyl acrylic amide, and N-methylol(meth)acrylic amide, a macromer manufactured by Toa Gosei Kagaku Kogyo which includes AS-6, AN-6, AA-6, AB-6, and AK-6, etc, vinyl compounds containing a phosphoric acid ester group which is a condensation product of hydroxyalkyl(meth)acrylates with phosphoric acid or a phosphate, and (meth)acrylates containing a urethane bond and a siloxane bond.

The acrylic polyol resin (A) may even contain a portion of a urethane bond and a siloxane bond in a main chain within a range not exceeding 50% (% by weight, hereinafter, the same) and, further, may even contain a unit derived from monomers other than (meth)acrylic acid derivatives. The monomers are not particularly limited and, as a specific example thereof, in addition to the monomers for introducing the functional groups, there are enumerated an aromatic hydrocarbon-based vinyl compound such as styrene, α -methylstyrene, chlorostyrene,

styrenesulphonic acid, and vinyltoluene; unsaturated carboxylic acid salts (an alkali metal salt, an ammonium salt, and an amine salt, etc.) of maleic acid, fumaric acid, and itaconic acid, etc.; unsaturated carboxylic acid esters such as a diester or a half ester of the unsaturated carboxylic acid with a linear or branched alcohol having a carbon number of 1-20; a vinyl ester such as vinyl acetate, vinyl propionate, and diallyl phthalate, and an allyl compound; vinyl compounds having amide group such as itaconic diamide, croton amide, maleic diamide, fumaric diamide, and N-vinylpyrrolidone; other vinyl compounds such as methylvinyl ether, cyclohexylvinyl ether, vinyl chloride, vinylidene chloride, chloroprene, propylene, butadiene, isoprene, fluoroolefine, maleimide, and vinyl sulphonic acid, etc.

As a polymerization method for the acrylic polyol resin (A), a usual polymerization method is employed and, a solution polymerization is particularly preferred from a viewpoint of easiness of synthesis, in which there is employed an azo-based radical initiator such as azobisisobutyronitrile. Molecular weight can be adjusted by using a chain transfer agent such as n-dodecyl mercaptan and t-dodecyl mercaptan or by controlling a reaction temperature.

(B) Acrylic copolymer containing an alkoxysilyl group

One of the acrylic copolymer (VII-B) (called also the component (VII-B)) containing an alkoxysilyl group is an acrylic copolymer containing at least one, preferably, at least two alkoxysilyl groups having a group shown by general formula (VII-2) described below in one molecule,



(in the formula, R^1 is an alkyl group having a carbon number of 1-10, R^2 and R^3 are a hydrogen atom or a monovalent hydrocarbon group selected from an alkyl group, aryl group, and aralkyl group which have a carbon number of 1-10, a is the number of a substituent group, and it is an integer of 0, 1, or 2).

Another one of the acrylic copolymer (VII-B) containing an alkoxysilyl group to be employed in the present invention is an acrylic copolymer containing an alkoxysilyl group, which has at least one, preferably, at least two groups shown by the above-described general formula (VII-2) at terminals or side chains in one molecule, and which has at least one group selected from an acid anhydride group, an epoxy group, an amino group, and carboxylic group.

In the general formula (VII-2), R^1 is more preferably an alkyl group of a carbon number of 1-4. In the case that the carbon number exceeds 10, or the R^1 is, for example, phenyl group or benzyl group other than the alkyl group, there lowers a reactivity in the alkoxysilyl group. As a specific example of the R^1 , there are enumerated methyl, ethyl, n-propyl, iso-propyl, n-butyl, and iso-butyl group, etc. As the alkyl group having a carbon number of 1-10 which is one kind of the R^2 , there are enumerated the same groups as in the R^1 and, as the aryl group, for example, there are enumerated phenyl group, tolyl group, xylyl group, etc., as the aralkyl group, for example, there is enumerated benzyl group, etc.

Since in the copolymer (VII-B), a main chain substantially consists of an acrylic copolymer chain, weatherability, solvent

resistance, and water resistance are improved in a cured article.

Further, since the alkoxysilyl group connects to carbon, water resistance, alkali resistance, and acid resistance, etc. are more improved.

The alkoxysilyl group reacts with hydroxyl group derived from the hydroxyalkyl (meth)acrylate monomer (a) modified by a small amount of lactones, and it contributes to crosslinking, and the alkoxysilyl group itself also reacts with each other, and it is a component for contributing to crosslinking. In the case that the number of the alkoxysilyl group in one molecule is less than 1 piece in the copolymer (VII-B), there lowers solvent resistance in physical properties of a coating layer.

The group selected from an acid anhydride group, an epoxy group, an amino group, and carboxylic group in the copolymer (VII-B) reacts with the group selected from an acid anhydride group, an epoxy group, an amino group, and carboxylic group in the acrylic polyol resin (VII-A) in a combination of the acid anhydride group/epoxy group, amino group/epoxy group, or carboxylic group/epoxy group, and it elevates solvent resistance and water resistance in a cured coating layer from the composition of the present invention.

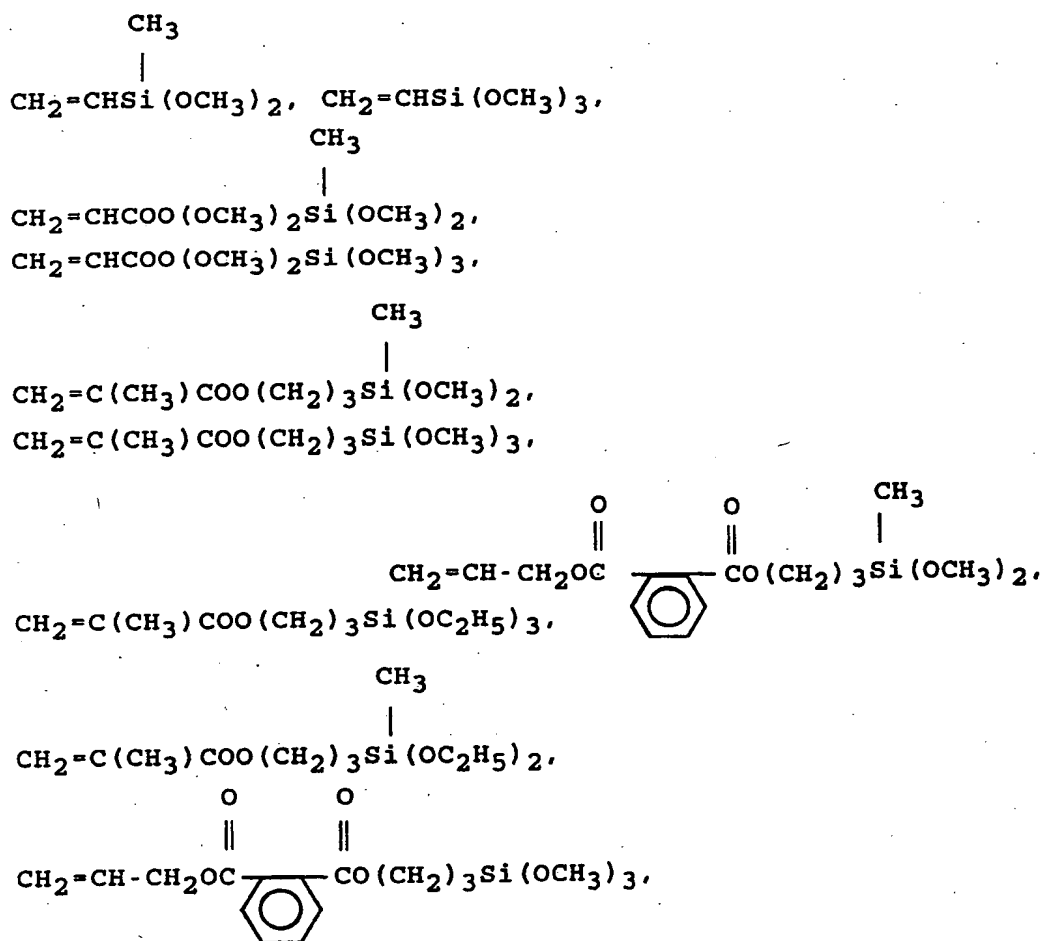
The number of the group selected from an acid anhydride group, an epoxy group, an amino group, and carboxylic group is not less than 1 piece per 1 molecule of the copolymer (VII-B) and, preferably 2-30 pieces from a viewpoint of solvent resistance and water resistance in the cured coating layer.

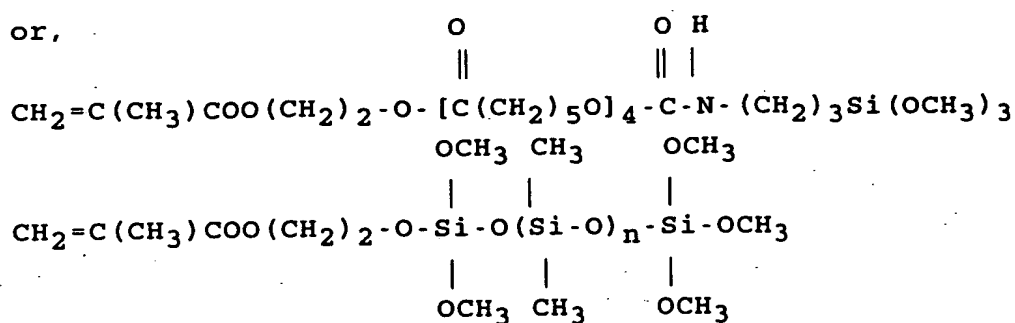
From a viewpoint of physical properties (strength, durability) of a coating layer, a number average molecular weight in the copolymer

(VII-B) is 1,000-30,000, and more preferably 3,000-25,000.

The copolymer (VII-B) can be obtained, for example, by copolymerization of a monomer (VII-b) containing the alkoxysilyl group with at least one of (meth)acrylic acid, and a derivative therefrom, or by copolymerization of a monomer (VII-b) containing the alkoxysilyl group with a monomer for introducing a functional group which is described later, (meth)acrylic acid, and a derivative therefrom.

The monomer containing the alkoxysilyl group is not particularly limited except that it has a polymerizable unsaturated double bond and the alkoxysilyl group represented by the above-described general formula (VII-2) and, as a specific example thereof, for example, there are enumerated the following compounds.





(n is 2-6)

There are enumerated (meth)acrylates having the alkoxysilyl group through urethane bond or a siloxane bond at terminal. These may be even solely or in combination of two or more kinds.

Proportion of the monomer containing the alkoxysilyl group is preferably 5-90% by weight, and more preferably 11-70% by weight in the copolymer (VII-B) from a viewpoint of curability of a composition and durability of a coating layer.

For introducing the acid anhydride group into the copolymer (VII-B), for example, there may be copolymerized the monomers exemplified for introducing the acid anhydride group, epoxy group, carboxylic group, and amino group into the acrylic polyol resin (VII-A).

The (meth)acrylic acid or derivatives thereof to be employed for introducing carboxylic group are not particularly limited and, as specific examples, there are enumerated methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, stearyl(meth)acrylate, benzyl(meth)acrylate, cyclohexyl(meth)acrylate, trifluoroethyl(meth)acrylate, pentafluoropropyl(meth)acrylate, perfluorocyclohexyl(meth)acrylate, (meth)acrylonitrile, (meth)acrylic amide, α -ethyl(meth)acrylic amide, N-butoxymethyl(meth)acrylic amide, N,N-dimethyl acrylic amide,

N-methyl acrylic amide, 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, N-methylol(meth)acrylic amide, Alonix M-5700 manufactured by Toa Gosei Kagaku Kogyo, a macromer manufactured by Toa Gosei Kagaku Kogyo which includes AS-6, AN-6, AA-6, AB-6, and AK-5, etc, Placel FA-1, Placel FA-A, Placel FM-1, and Placel FM-4, etc. manufactured by Daicel Chemical Industries, Ltd., vinyl compounds containing a phosphoric acid ester group which is a condensed product of hydroxyalkyl(meth)acrylates with phosphoric acid or a phosphate, and (meth)acrylates containing a urethane bond and a siloxane bond, etc.

Further, the copolymer (B) may even contain units of a urethane bond and a siloxane bond in a main chain within a range not exceeding 50% and, further, may even contain units of monomers other than (meth)acrylic acid derivatives.

The monomers are not particularly limited and, as a specific example thereof, in addition to the above-described monomers for introducing functional groups, there are enumerated an aromatic hydrocarbon-based vinyl compound such as styrene, α -methylstyrene, chlorostyrene, styrenesulphonic acid, 4-hydroxystyrene, and vinyltoluene; unsaturated carboxylic acid salts (an alkali metal salt, an ammonium salt, and an amine salt, etc.) such as maleic acid, fumaric acid, and itaconic acid, unsaturated carboxylic acid esters such as a diester or a half ester of the unsaturated carboxylic acid with a linear or branched alcohol having a carbon number of 1-20; a vinylester such as vinyl acetate, vinyl propionate, and diallyl phthalate, and an allyl compound; vinyl compounds having amide group such as itaconic diamide, croton amide, maleic diamide, fumaric diamide, and

N-vinylpyrrolidone; other vinyl compounds such as 2-hydroxyethylvinyl ether, methylvinyl ether, cyclohexylvinyl ether, vinyl chloride, vinylidene chloride, chloroprene, propylene, butadiene, isoprene, a fluoroolefine, maleimide, and vinyl sulphonic acid, etc.

The copolymer (VII-B) can be obtained, for example, by a method shown in JP-A-54036395 Official Gazette, etc., and a solution polymerization method is most preferred from a viewpoint of easiness of synthesis, in which there is employed an azo-based radical initiator such as azobisisobutyronitrile.

In the solution polymerization method, a molecular weight can be adjusted by using a chain transfer agent such as n-dodecyl mercaptan, t-dodecyl mercaptan, n-butyl mercaptan, γ -mercaptopropyl trimethoxysilane, γ -mercaptopropyl triethoxysilane, γ -mercaptopropyl methyldimethoxysilane, γ -mercaptopropyl methyldiethoxysilane, $(\text{CH}_3\text{O})_3\text{-Si-S-S-Si-(OCH}_3)_3$, and $(\text{CH}_3\text{O})_3\text{-Si-S}_8\text{-Si-(OCH}_3)_3$. Particularly, the alkoxysilyl group can be introduced in terminals of a polymer by using the chain transfer agent having the alkoxysilyl group in the molecule, for example, γ -mercaptopropyl trimethoxysilane.

As solvents to be employed in the solution polymerization, there may be employed the solvents to be employed in the preparation of the acrylic polyol resin in the present invention I.

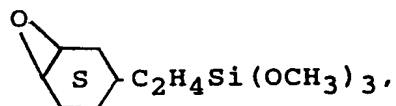
As use proportion of the component (VII-A) with respect to the component (VII-B), the component (VII-A)/the component (VII-B) is preferably (2-50)/(30-80) by weight ratio. In the case that the component (VII-A)/the component (VII-B) exceeds the above range,

physical properties such as water resistance lowers in a coating layer and, in the case of less than the above range, there does not become sufficiently obtained an effect for improving an outer appearance and hardness of a coating layer by adding the component (VII-A).

In the component (VII-A) and the component (VII-B), reactive functional groups are separately contained in combination of the acid anhydride group/epoxy group; the amino group/epoxy group; and carboxylic group/epoxy group, and the combination may contain one, or two or more combination.

(C) Catalyst for curing (VII-C)

As the catalyst for curing (VII-C) to be employed in the present invention, for example, there are enumerated an organic tin compound such as dibutyltin dilaurate, dibutyltin dilmaleate, dioctyltin dilaurate, dioctyltin dimaleate, and tin octylate; phosphoric acid or a phosphate such as monomethyl phosphate, monoethyl phosphate, monobutyl phosphate, monooctyl phosphate, monodecyl phosphate, dimethyl phosphate, diethyl phosphate, dibutyl phosphate, dioctyl phosphate, didecyl phosphate; propyleneoxide, butyleneoxide, cyclohexeneoxide, glycidylmethacrylate, glycidol, acrylic glycidylether, γ -glycidoxypropyl trimethoxysilane, γ -glycidoxypropyl triethoxysilane, γ -glycidoxypropyl methyldimethoxysilane, a compound shown by a formula described below,



Kardula E manufactured by Yuka Shell Epoxy, Ltd., an adduct of an epoxy compound with a phosphoric acid and/or an acidic monophosphate such as Epikote 828 and Epikote 1001 manufactured by Yuka Shell Epoxy, Ltd.;

organic titanate compounds; organic aluminum compounds; acidic compounds such as maleic acid and paratoluene sulphonic acid; amines such as hexyl amine, di-2-ethyl hexyl amine, N,N-dimethyldodecylamine, and dodecyl amine; a mixture or reaction product of the amines with the acidic phosphates; and alkali compounds such as sodium hydroxide and potassium hydroxide, etc.

Of the catalysts for curing (VII-C), there are preferred the organic tin compound, acidic phosphates, mixture or reaction product of the amines with the acidic phosphates, saturated or unsaturated polyvalent carboxylic acid or anhydride thereof, reactive silicone compound, organic titanate compounds, organic aluminum compounds, or a mixture thereof because of a high activity. Such the catalysts for curing (VII-C) may be employed solely or even in combination of two or more kinds.

Use amount of the catalysts for curing (VII-C) is not particularly limited, and it is usually 0.1-20 parts, and preferably 1-10 parts based on 100 parts of solid content of the component (VII-A) and the component (VII-B). In the case that the use amount of the components (VII-C) is less than 0.1 parts, curability tends to lower and, in the case of exceeding 20 parts, physical properties (an outer appearance) in a coating layer tend to lower.

(D) Other additives (VII-D)

In the composition of the present invention, a dehydrating agent may be optionally added and, there can be ensured a stability, a stability not including any problems even though being repeatedly employed over a long time of period by using the dehydrating agent.

As the dehydrating agent, for example, there are enumerated

hydrolyzable ester compounds such as ortho methylformate, ortho ethylformate, ortho methylacetate, ortho ethylacetate, methyltrimethoxy silane, γ -methacryloxypropyl trimethoxy silane, vinyltrimethoxy silane, methyl silicate, and ethyl silicate.

The above hydrolyzable ester compounds may be added before polymerization, after polymerization, and during polymerization of the copolymer (VII-B) containing the alkoxysilyl group.

Use amount of the dehydrating agent is not particularly limited and, it is usually not more than 100 parts by weight, and preferably not more than 50 parts by weight based on 100 parts by weight of solid components in the component (VII-A) and the component (VII-B).

Further, by simultaneously employing an accelerating agent for the dehydrating agent, an effect by the dehydrating agent can be elevated.

As the accelerating agent for the dehydrating agent, for example, there are enumerated an inorganic acid such as hydrochloric acid, sulphuric acid, phosphoric acid, and sulphuric acid; an organic acid such as formic acid, acetic acid, oxalic acid, benzoic acid, phthalic acid, paratoluene sulphonic acid, acrylic acid, and methacrylic acid; a metal salt of carboxylic acid such as an alkyl titanate and lead octylate; a carboxylic acid type organic tin compound such as tin octylate, dibutyltin dilaurate and dioctyltin dimaleate; a sulphide compound such as monobutyltin sulphide and dioctyltin mercaptide, and a mercaptide type organic compound; an organic tin oxide such as dioctyltin oxide; an organic tin compound by a reaction of the organic tin oxide with an ester compound such as ethylsilicate, ethylsilicate 40, dimethylmaleate and dioctyl phthalate; an amine such as

tetraethylene pentamine, triethylene diamine, and N- β -aminoethyl- γ -aminopropyl trimethoxy silane; an alkali catalyst such as potassium hydroxide and sodium hydroxide, etc., and the organic acid, inorganic acid and the organic tin compound are preferred.

The accelerator for the dehydrating agent is employed in 0.0001-20 parts by weight, and preferably 0.001-10 parts by weight based on 100 parts by weight of the dehydrating agent. In the case of employing a compound which is also the above-described component (VII-C) as the accelerator for the dehydrating agent, it is employed in use amount of the component (VII-C).

In the composition of the present invention, a solvent may be added and, nonreactive solvents are preferably employed.

As specific examples of such the solvents, for example, there are enumerated an aliphatic hydrocarbon solvent which is employed for a usual coating and a coating agent, aromatic hydrocarbons, chlorinated hydrocarbons, alcohols, ketones, esters, ethers, alcohol esters, ketone alcohols, ether alcohols, ketone ethers, ketone esters, and ester ethers, etc. Of those, in the case that there is employed a solvent including an alkyl alcohol, a stability is preferably improved in the composition of the present invention.

As the alkyl alcohol, there is preferred an alcohol having a carbon number of 1-10 in the alkyl group and, for example, there are employed methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol, n-amino alcohol, isoamyl alcohol, hexyl alcohol, octyl alcohol, and cellosolves, etc.

Use amount of the alcohols is not particularly limited, and it is not more than 100 parts by weight, and preferably not more than 50 parts by weight based on 100 parts by weight of solid components of the components (VII-A) and (VII-B).

By employing an alcohol, particularly, an alkyl alcohol together with the dehydrating agent, there is observed a remarkable effect in a storage stability in the case that there are stored by mixing the components (VII-A), (VII-B), and (VII-C) in the composition of the present invention.

Use amount of the solvents depends upon a molecular weight or composition of the components (VII-A) and (VII-B), and it is adjusted by fitting to a solid component concentration or viscosity to be practically required.

In order to improve characteristics such as adhesion, hardness, and solvent resistance, there may be even added a hydrolyzable silane compound, a condensate thereof, a reaction product thereof, or a mixture thereof in the composition of the present invention.

As specific examples of the hydrolyzable silane compound, for example, there are enumerated methylsilicate, methyltrimethoxy silane, ethyltrimethoxy silane, butyltrimethoxy silane, octyltrimethoxy silane, dodecyltrimethoxy silane, phenyltrimethoxy silane, vinyltrimethoxy silane, γ -methacryloxypropyl trimethoxy silane, γ -acryloxypropyl trimethoxy silane, γ -glycidoxypropyl trimethoxy silane, γ -mercaptopropyl trimethoxy silane, γ -aminopropyl trimethoxy silane, N- β -aminoethyl- γ -propyl trimethoxy silane, dimethyldimethoxy silane, diethyldimethoxy silane, dibutyldimethoxy

silane, diphenyldimethoxy silane, vinylmethyldimethoxy silane, γ -methacryloxypropyl methyl dimethoxysilane, trimethylmethoxysilane, triethylmethoxy silane, triphenylmethoxy silane, ethyl silicate, methyltriethoxysilane, ethyltriethoxy silane, butyltriethoxy silane, octyltriethoxy silane, dodecyltriethoxy silane, phenyltriethoxy silane, vinyltriethoxy silane, γ -methacryloxypropyl triethoxy silane, γ -acryloxypropyl triethoxy silane, γ -glycidoxypropyl triethoxy silane, γ -mercaptopropyl triethoxy silane, γ -aminopropyl triethoxy silane, N- β -aminoethyl- γ -propyl triethoxy silane, dimethyl diethoxy silane, diethyl diethoxy silane, dibutyl diethoxy silane, diphenyl diethoxy silane, vinylmethyldiethoxy silane, γ -methacryloxypropyl methyldiethoxysilane, trimethylethoxysilane, triethylethoxy silane, and triphenylmethoxy silane, etc.

Further, a condensate such as a partially-hydrolyzed condensate of the silane compounds can be readily obtained by the silane compounds solely or in combination and adding necessary amount of water and, optionally adding a small amount of catalysts for condensation such as hydrochloric acid and sulphuric acid, while maintaining at from an ordinary temperature to 100°C, followed by proceeding while removing an alcohol produced. For example, as a compound containing methoxysilyl group which is a partially-hydrolyzed condensate of methyl silicate, there are enumerated Methyl Silicate 47, Methyl Silicate 51, Methyl Silicate 55, Methyl Silicate 58, and Methyl Silicate 60 manufactured by Nihon Kolcoat Kagaku, Ltd., etc.

As the compound containing methoxysilyl group which is a partially-hydrolyzed condensate of methyl trimethoxy silane and dimethyl dimethoxy silane, there are enumerated AFP-1, AFP-2, AFP-6,

KP213, KR217, and KR9218 manufactured by Shin-etsu Kagaku Kogyo, Ltd.: TSR165 and TR3357 manufactured by Toshiba Silicone, Ltd.: Y-1587, FZ3701, and FZ3704 manufactured by Nihon Unicar, Ltd., etc.

Further, as the compound containing ethoxysilyl group which is a partially-hydrolyzed condensate of ethyl silicate, there are enumerated Ethyl Silicate 40, HAS-1, HAS-6, and HAS-10 manufactured by Nihon Kolcoat, Ltd., etc.

As the reaction product of the hydrolyzable silane compound, for example, there are enumerated a reaction product of a silane coupling agent containing amino group with a compound containing an epoxy group, a reaction product of a silane coupling agent containing amino group with a silane coupling agent containing an epoxy group such as ethyleneoxide, butyleneoxide, epichlorohydrin, an epoxidized soybean oil, Epikote 828 and Epikote 1001 manufactured by Yuka Shell Epoxy, Ltd.; a reaction product of a silane coupling agent containing an epoxy group with aliphatic amines such as ethyl amine, diethyl amine, triethyl amine, ethylene diamine, hexane diamine, diethylene triamine, triethylene tetramine, and tetraethylene pentamine, aromatic amines such as aniline and diphenyl amine, cycloaliphatic amines such as cyclopentyl amine and cyclohexyl amine, amines such as ethanolamine, etc.

There is not particularly limited use amount of the hydrolyzable silane compound, the condensate thereof, the reaction product thereof, and a mixture thereof, and it is generally not more than 100 parts by weight, and preferably not more than 50 parts by weight based on 100 parts by weight of solid components of the components (VII-A) and (VII-B).

In the composition of the present invention, a polyorganosiloxane may be added in order to give a water repellent property to a cured coating layer. The polyorganosiloxane, if it has a reactive functional group and is compatible with the hydroxyl group-contained polymer (VII-A) and the component (VII-B), can be freely selected and is not particularly limited.

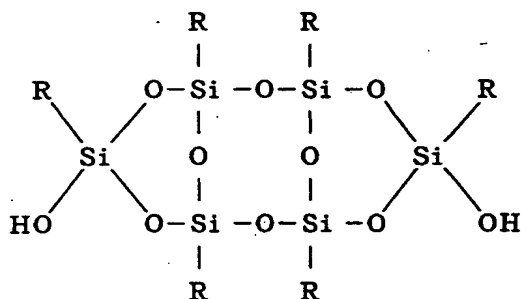
Structure of the polyorganosiloxane may be in any of linear, branched, net-like, and cyclic in a structure and, as an organo group, there are enumerated hydrogen atom, an alkyl group, an alkenyl group, and an aryl group, methyl group, ethyl group, propyl group, butyl group, hexyl group, allyl group, and phenyl group, etc. Of the organo groups, methyl group and phenyl group are practically advantageous because of being industrially prepared and low in price.

As the reactive functional groups, there are preferred a silanol group, an alkoxysilyl group, an alcoholic hydroxyl group, glycidyl group, amino group, mercapto group, carboxylic group, amide group, vinyl group, and (meth)acryloxy group and. Of those, the silanol group, the alkoxysilyl group, and alcoholic hydroxyl group are preferred.

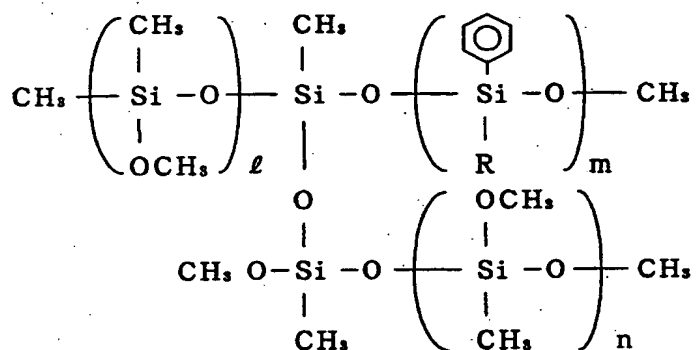
In the polyorganosiloxane, the number of the reactive functional groups is preferably not less than 1 piece in one molecule. In the polyorganosiloxane, although a molecular weight can be freely selected if it is a range having compatibility, since compatibility lowers in a higher molecular weight, silicone atom is preferred in 2-300 pieces, and it is more preferred in 2-100 pieces, and it is particularly preferred in 3-50 pieces.

As a specific example of such the polyorganosiloxane, for example, there are enumerated a silicone rubber, a silicone varnish, a reactive

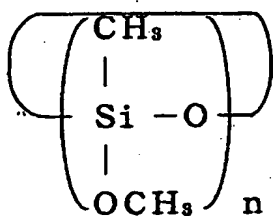
polydimethylsiloxane employed as an intermediate for modifying an organic polymer and a reactive silicone oil, and a reactive polydiphenyl siloxane, a reactive polymethylphenyl siloxane, which is a copolymerized type of dimethyl with diphenyl,



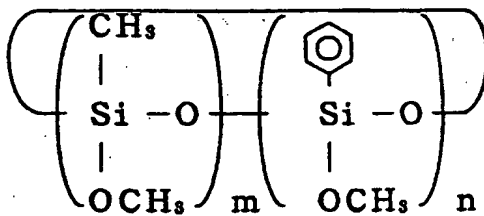
(in the formula, R is a group selected from the group consisting of a phenyl group, an alkyl group having a carbon number of 1-4, and hydroxyl group),



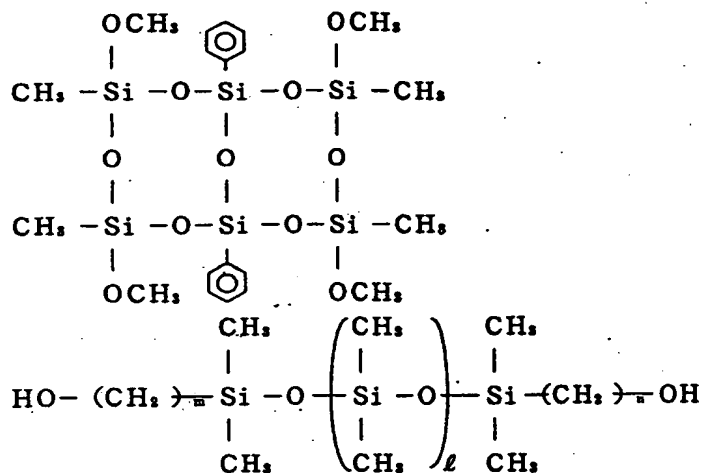
(in the formula, R is a group selected from the group consisting of a phenyl group, an alkyl group having a carbon number of 1-4, and hydroxyl group, and l, m, and n are 1-5, respectively),



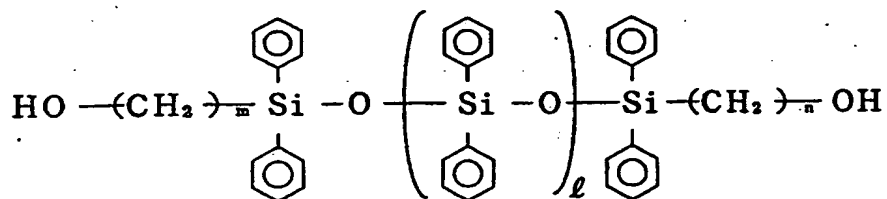
(n is 2-20)



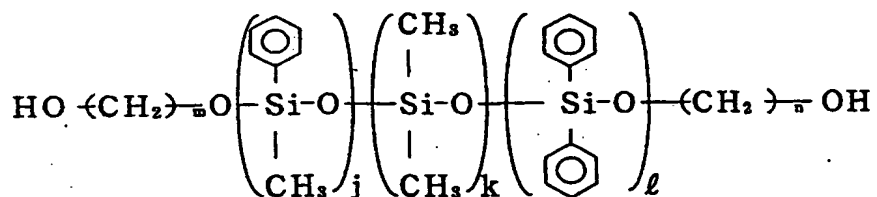
(m and n are 1-10, respectively)



(l is 0-100, m and n are 1-3, respectively)



(l is 0-100, m and n are 1-3, respectively)



Use amount of the polyorganosiloxane is generally not less than 100 parts, and preferably not less than 50 parts based on 100 parts of solid components in the components (VII-A) and (VII-B).

In the composition of the present invention, there may be even added additives such as a diluent, pigments (including an extender pigment), an ultraviolet ray absorbent, an anti-sedimentation agent, a leveling agent; celluloses such as a nitrocellulose, and a cellulose acetate butylate; and a resin such as an epoxy resin, a melamine resin,

a vinylchloride resin, a chlorinated polyolefin, a chlorinated rubber, a polyvinyl butylal, an alkyd resin, an oil-free alkyd resin, an acrylic-modified alkyd resin, an acrylic resin, a fluorine resin having hydroxyl group, a polyester polyol, a polyether polyol, and a polyurethane polyol, etc.

Hereinafter, there is illustrated a method for the preparation of the composition in relation to the present invention.

The composition of the present invention is composed of the above-described components is not particularly limited, for example, it is prepared by cold-blending of the components (VII-A) and (VII-B), or mixing the components (VII-A) and (VII-B) and after that, heating (hot-blending) to obtain a partially reacted product, and mixing the product with the component (VII-C).

The composition of the present invention can be cured by heating at not less than 30°C, and preferably 55-35°C after coating on a body to be coated by usual methods using, for example, dipping, spraying, brushing, and a roll coating or a flow coater.

The thermosetting composition of the present invention is useful as a coating, an adhesive, a sealant, and a modifier for plastics, and in the case of employing as the coating, it can provide a coating layer which is excellent in weatherability, adhesion, and hardness and, moreover, which is excellent in durability.

Hereinafter, a coated body of the present invention will be illustrated.

In the coated body of the present invention, there is coated a coating containing metallic powder and/or coloring pigments (a coating

containing the metallic powder is called a metallic base coating, and a coating containing the coloring pigments is called a solid color coating), and since a top clear coating (a thermosetting coating) primarily containing the above-described the thermosetting composition is coated on a coated surface, it is a coated body which is excellent in weatherability, acid resistance, and staining resistance, etc.

The coating containing metallic powder and/or coloring pigments is not particularly limited and, for example, there are enumerated compounds primarily containing an amino alkyd resin, an oil-free alkyd resin, a thermosetting acrylic resin, a thermosetting urethane resin, a nitrocellulose lacquer, a modified acrylic lacquer, a straight acrylic lacquer, a ordinary temperature-curable urethane resin, an acrylic enamel resin, an oxidation-curable modified alkyd resin (CAB, etc.), an ordinary temperature- or thermally-curable type fluorine resin, a resin containing a hydrolyzable silyl group, and a mixture of a resin containing a hydrolyzable silyl group with a vinyl-based copolymer having hydroxylic group, etc.

Further, as a type of the coating, there may be even any one of a solution type coating containing an organic solvent as a medium, a nonaqueous dispersion coating, a multi-liquid type coating, a powder coating, a slurry coating, and a water-based coating, etc.

The above-described metallic powder and coloring pigments may be even publicly-known, and there may be even any one of metallic powder and coloring pigments.

As the metallic powder, for example, there are enumerated aluminum powder, copper powder, and mica powder, etc., and, as the coloring

pigments, for example, there are enumerated organic-based pigments such as Phthalocyanine Blue, Toluidine Red, and Benzidine Yellow, and inorganic-based pigments such as titanium oxide, carbon black, and iron oxide red, etc. The metallic powder and coloring pigments may be employed solely or in combination of two or more kinds.

In the coating containing the metallic powder and/or coloring pigments, weatherability can be more improved by employing an ultraviolet ray absorbent and a photostabilizer.

As the ultraviolet ray absorbent, conventionally-known ones can be widely employed, for example, there is preferred an ultraviolet ray absorbent such as a benzophenone-based one, a triazole-based one, a phenylsalicylate-based one, a diphenylacrylate-based one, and an acetophenone-based one.

As the photostabilizer, conventionally-known ones can be widely employed, for example, there are enumerated bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, 2-(3,5-di-tert-butyl-4-hydroxybenzyl)2-n-butyl malooate bis(1,2,2,6,6-pentamethyl-4-piperidyl), tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane tetracarboxylate, and tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)-1,2,3,4-butane tetracarboxylate, etc. These may be employed solely or even in combination of two or more kinds.

In the coating containing the metallic powder and/or coloring pigments, there may be even added the above-described silane compounds, condensates thereof, reaction product thereof, and a mixture thereof

in order to elevate adhesion to a coating layer and a top clear coating layer.

Addition amount thereof is usually not more than 50 parts, and preferably not more than 20 parts in 100 parts of the coating containing the metallic powder and/or coloring pigments.

By formulating the above-described ultraviolet ray absorbent or photostabilizer with the top clear coating, weatherability is remarkably improved. Further, weatherability can be more improved by employing the ultraviolet ray absorbent together with the photostabilizer.

The formulating amount of the ultraviolet ray absorbent is usually 0.1-10 parts, and preferably 1-5 parts based on 100 parts of solid components in the top clear coating. Further, the formulating amount of the photostabilizer is usually 0.1-10 parts, and preferably 1-5 parts based on 100 parts of solid components in the top clear coating.

A method for the preparation of the body to be coated of the present invention is not particularly limited and, for example, it can be prepared by a method (two coat-one bake style) in which after coating the coating containing the metallic powder and/or coloring pigments and setting for several minutes, the top clear coating is coated by a wet-on-wet style, followed by thermally curing, and a method (two coat-two bake style) in which after coating the coating containing the metallic powder and/or coloring pigments and thermally curing, the top clear coating is coated and thermally cured.

Thickness of a coating layer is not also particularly limited and, thickness of a coating layer containing the metallic powder (or) coloring pigments is preferably 10-30 μm from a viewpoint of concealing,

and thickness of the top clear coat is preferably 20-50 μm from a viewpoint of durability.

Thus-prepared coating layer shows an excellent property in a specific characteristic such as outer appearance and weatherability.

As an object for forming the coating layer, for example, there are enumerated buildings, cars, industrial machines, steel-made furniture, home electric appliances, and plastics products, etc., and the coating is employed for finishing as an over coating.

Hereinafter, the present invention No. VIII is illustrated.

The hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactone in which a proportion of monomers having two or more continuous chains ($n \geq 2$) of lactone represented by the above-described general formula (I) to be employed in the present invention is less than 50% is as illustrated in the present invention No. I.

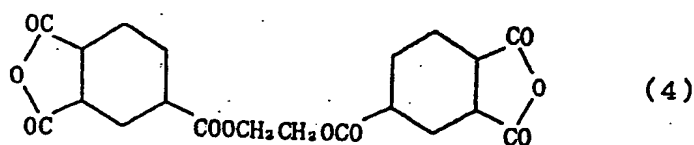
By allowing to react the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactone represented by the above-described general formula (I) with the carboxylic acid represented by the above-described general formula (VIII-2) or the anhydride thereof (VIII-b), there is obtained the hydroxyalkyl(meth)acrylate composition (a') having carboxylic group modified by a small amount of lactone represented by the above-described general formula (VIII-3).

As the carboxylic acid represented by the general formula (VIII-2) or the anhydride thereof (VIII-b), for example, there can be enumerated malonic acid, succinic acid, glutaric acid, adipic acid, sberic acid,

azelaic acid, sebacic acid, brasilic acid, maleic acid, fumaric acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, trimerritic acid, tartaric acid, malic acid, mannose acid, 1,4-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid, hexahydrophthalic acid, galactose acid, 4,5-cyclohexene dicarboxylic acid, 3,6-methylene-4-cyclohexene-1,2-dicarboxylic acid, citric acid, pyromellitic acid, dimer of phthalic anhydride, diphenylether tetracarboxylic acid, diphenylsulphone tetracarboxylic acid, benzophenone tetracarboxylic acid, butane-1,2,3,4-tetracarboxylic acid, anhydrides thereof, and a mixture thereof. Of those, maleic anhydride, phthalic anhydride, trimerritic anhydride, and pyromerritic anhydride are preferred as a raw material for the present invention because of readily obtaining.

The carboxylic acid may be unsubstituted or can be also substituted by optional groups by which a reaction is not significantly disturbed. Examples of appropriate substituent groups include a halogen, nitro, alkoxy, alkyl, and carbonyl group, etc. Further, a desired product can be prepared by allowing to react an acid chloride which is the component (VIII-b) with a lactone(meth)acrylate.

Otherwise, residual carboxylic group (R^9 in the general formula (VIII-2)) of the acid anhydride may contain an inert functional group such as ether, ester, halogen, and ketone, and, for example, there can be employed an ethyleneglycol ester of trimellitic anhydride (Ricacid TMEG™ (manufactured by Shinnihon Rika)) represented by general formula (4) described below, etc.



By employing an anhydride of a polyvalent carboxylic having at least two carboxylic groups in the molecule, since one carboxylic group of the polyvalent carboxylic acid qualitatively reacts with hydroxyl group at terminal of the hydroxyalkyl (meth)acrylate composition (a) modified by a small amount of lactone, one carboxylic group of the polyvalent carboxylic acid can be controlled so as to add to hydroxyl group at a terminal group.

As a result, there can become obtained the (meth)acrylate compound (a', VIII-3) containing at least one carboxylic group in the molecule in a high selectivity.

A reaction of the above-described component (a) with the component (VIII-b) slowly proceeds at a low temperature and, a polymerization of (meth)acryloyl group is caused at a high temperature. Accordingly, a preferred temperature ranges in 40-160°C.

In order to prevent the polymerization of (meth)acryloyl group, the reaction is preferably conducted under the presence of oxygen and, further, it is preferably conducted under the presence of, for example, a polymerization inhibitor such as hydroquinone monomethylether. The polymerization inhibitor such as quinones is employed in an amount of not more than 5,000 ppm, and preferably not more than 700 ppm in a reaction mass.

Although the reaction proceeds under the absence of a catalyst, the catalyst may be even optionally employed. As the catalyst, there

are enumerated a basic compound such as triethylamine, pyridine, N-methylimidazole, diazabicycloundecene, and diazabicyclooctane; an ammonium salt such as trimethylbenzyl ammonium chloride and tetrabutyl ammonium bromide; and a publicly-known catalyst such as other acids and alkalis, etc.

Although the reaction may be conducted under the absence of a solvent, the solvent may be even employed. As the solvent, there are enumerated toluene, methylethyl ketone, ethyl acetate, and 1-methoxy-2-acetoxyp propane, etc. Further, there may be employed a reactive diluent such as a polyethyleneglycol monomethylether mono(meth)acrylate or a polyethyleneglycol di(meth)acrylate which are a mono or poly(meth)acrylate.

Feeding ratio of the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactone with the carboxylic acid or the anhydride (VIII-b) is preferably 0.9-1.1 by mol. In the case that molar ratio of the component (VIII-b) exceeds 1.1, there remains a large amount of the component (VIII-b) and, in uses in which an epoxy compound is formulated, a pot-life is unpreferably shortened. Further, in the case of less than 0.9, a high molecular weight diesters or triesters, etc. are by-produced, unpreferably resulting in that a viscosity becomes high.

Method for the preparation according to the present invention can be advantageously conducted by industrial fashion and, moreover, a lactone acrylate compound having carboxylic group obtained is effective for improvement of adhesion to materials such as a resin having amino groups which includes a nylon, an inorganic compound which includes a metal and silica having hydroxyl group and, further, it

is exceedingly useful as a raw material for resins, which is effective for solubility of an acrylic resin to water and an aqueous alkali solution, above all, for shortening a developing time of period in an alkali development step when preparing a pattern in which curing by an ultraviolet ray is utilized, and for a removal property of an uncured portion.

Subsequently, the present invention No. IX is illustrated hereinafter in detail.

I. Raw material for a curable resin composition

First of all, there are illustrated raw materials to be employed for preparation of the curable resin composition in relation to the present invention.

I-1. <Acrylic polycarboxylic acid resin (A')>

The acrylic polycarboxylic acid resin (A') to be employed for the curable resin composition of the present invention has at least two carboxylic groups on average, 5-300 mgKOH/g of an acid value, and preferably 25-250 mgKOH/g, more preferably 50-200 mgKOH/g, 500-8000 of a number average molecular weight, preferably 800-6000, and more preferably 1500-4000.

The acrylic polycarboxylic acid resin (A') is obtained by copolymerizing 5-80% by weight of an ethylenic unsaturated monomer having carboxylic group (a1), provided that a ratio of the hydroxyalkyl(meth)acrylate composition (a') having carboxylic group modified by a small amount of lactone is 5-50% by weight in the ethylenic unsaturated monomer having carboxylic group (a1), with 20-95% by weight of an ethylenic unsaturated monomer not having carboxylic group (a2) according to publicly-known methods.

In the case that the monomer (a') is less than 5% by weight, a coating layer becomes unpreferably hard and, in the case of exceeding 50% by weight, water resistance becomes unpreferably worse.

Further, in the case that the monomer (a1) exceeds 80% by weight, a coating layer becomes unpreferably hard and brittle, and in the case that the monomer (a2) exceeds 95% by weight, curing becomes unpreferably insufficient.

Proportion of the monomer (a') which constructs the acrylic polycarboxylic acid resin (A') is 5-50% by weight, and preferably 10-40% by weight.

Copolymerization can be conducted using an azo-based radical initiator or a peroxide-based initiator as a radical polymerization initiator in an amount of 0.5-15 parts by weight based on 100 parts by weight of total monomers, and at a polymerization temperature of 80-200°C and a polymerization period of 3-10 hours, and under an ordinary pressure or compressurization. In the case, there may be even added a chain transfer agent and an agent for preventing discoloration, etc.

Further, in the present invention, there may be even employed an acrylic polycarboxylic acid resin (bA') in which terminal carboxylic groups in the acrylic polycarboxylic acid resin (A') are blocked by a block group which produces carboxylic group by heating and/or water, in place of the acrylic polycarboxylic acid resin (A').

I-1-1 <Hydroxyalkyl(meth)acrylate composition (a') having carboxylic group modified by a small amount of lactone>

The hydroxyalkyl(meth)acrylate composition (a') having carboxylic group modified by a small amount of lactone to be employed

for the acrylic polycarboxylic acid resin (A') is a composition obtained by allowing to react the hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactone represented by the above-described general formula (1) with the carboxylic acid represented by the above-described general formula (VIII-2) or the anhydride thereof (VIII-b), and the composition is represented by the above-described general formula (VIII-3).

(1) <Hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactone>

The hydroxyalkyl(meth)acrylate composition (a) modified by a small amount of lactone represented by the above-described general formula (1) is as illustrated in the present invention No. I.

(2) <Carboxylic acid or anhydride thereof>

The carboxylic acid represented by the above-described general formula (VIII-2) or the anhydride thereof is as illustrated in the present invention No. VIII.

For example, there can be enumerated malonic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, azelaic acid, sebacic acid, brasilic acid, maleic acid, fumaric acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, tartaric acid, malic acid, mannose acid, 1,4-cyclohexane dicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid, hexahydrophthalic acid, galactose acid, 4,5-cyclohexene dicarboxylic acid, 3,6-methylene-4-cyclohexene-1,2-dicarboxylic acid, citric acid, pyromellitic acid, dimer of phthalic anhydride, diphenylether tetracarboxylic acid, diphenylsulphone tetracarboxylic acid,

benzophenone tetracarboxylic acid, butane-1,2,3,4-tetracarboxylic acid, anhydrides thereof, and a mixture thereof. Of those, maleic anhydride, phthalic anhydride, trimellitic anhydride, and pyromellitic anhydride are preferred as a raw material for the present invention because of readily obtaining.

The carboxylic acid may be unsubstituted or can be also substituted by optional groups by which a reaction is not significantly disturbed. Examples of appropriate substituent groups include a halogen, nitro, alkoxy, alkyl, and carbonyl group, etc. Further, a desired product can be prepared by allowing to react an acid chloride with a lactone (meth)acrylate.

Otherwise, residual carboxylic group (R^6 in the general formula (2)) in the acid anhydride may even contain an inert functional group such as ether, ester, halogen, and ketone, and, for example, there can be employed an ethyleneglycol ester of trimellitic anhydride (Ricacid TMEGTM (manufactured by Shinnihon Rika)), etc.

By employing an anhydride of a polyvalent carboxylic acid having at least two carboxylic groups in the molecule, since one carboxylic group in the polyvalent carboxylic acid qualitatively reacts with hydroxyl group at a terminal of the hydroxyalkyl (meth)acrylate composition (a) modified by a small amount of lactone, one carboxylic group of the polyvalent carboxylic acid can be controlled so as to add to hydroxyl group at a terminal group.

As a result, the hydroxyalkyl (meth)acrylate composition (a') modified by lactone containing carboxylic group can become obtained in a high efficiency.

A reaction of the above-described component (a) with the carboxylic acid or the anhydride thereof slowly proceeds at a low temperature and, a polymerization of (meth)acryloyl group is caused at a high temperature. Accordingly, a preferred temperature ranges in 40-160°C.

In order to prevent the polymerization of (meth)acryloyl group, the reaction is preferably conducted under the presence of oxygen and, it is preferably conducted under the presence of, for example, a polymerization inhibitor such as hydroquinone monomethylether. The polymerization inhibitor such as quinones is employed in an amount of not more than 5,000 ppm, and preferably not more than 700 ppm in a reaction mass.

Although the reaction proceeds under the absence of a catalyst, the catalyst may be even optionally employed. As the catalyst, there are enumerated a basic compound such as triethylamine, pyridine, N-methylimidazole, diazabicycloundecene, and diazabicyclooctane; an ammonium salt such as trimethylbenzyl ammonium chloride and tetrabutyl ammonium bromide; and a publicly-known catalyst such as other acids and alkalis, etc.

The reaction may be conducted under the absence of a solvent and, the solvent may be even employed. As the solvent, there are enumerated toluene, methylethyl ketone, ethyl acetate, and 1-methoxy-2-acetoxyp propane, etc. Further, there may be employed a reactive diluent such as a polyethyleneglycol monomethylether mono(meth)acrylate or a polyethyleneglycol di(meth)acrylate which are a mono or poly(meth)acrylate as a solvent.

Feeding ratio of the hydroxyalkyl(meth)acrylate composition (a)

modified by a small amount of lactone with the carboxylic acid or the anhydride is preferably 0.9-1.1 by mol. In the case that molar ratio of the carboxylic acid or the anhydride exceeds 1.1, residual amount thereof becomes large and, in uses in which an epoxy compound is formulated, a pot-life is unpreferably shortened.

Further, in the case of less than 0.9, high molecular weight diesters or triesters, etc. are by-produced, unpreferably resulting in that a viscosity becomes high.

I-1-2. <Ethylenic unsaturated monomer (a1) having carboxylic group>

As the ethylenic unsaturated monomer (a1) having carboxylic group which is other monomer component to be employed for copolymerization of the above-described acrylic polycarboxylic acid resin (A'), for example, there are enumerated acrylic acid, methacrylic acid, itaconic acid, maleic acid, and an adduct of ϵ -caprolactone therewith (for example, "Alonix M-5300" manufactured by Toa Gosei Kagaku, Ltd.), an adduct of the ethylenic unsaturated monomer (d3) having hydroxyl group represented by the above-described general formula (4) with the carboxylic acid or the anhydride, and an adduct of an ethylenic unsaturated monomer (f) having an acid anhydride group with a monoalcohol (g). These may be employed solely or in combination of two or more kinds.

The carboxylic acid or the anhydride to be employed herein, if it is a compound capable of providing a carboxylic functional property by a half esterification reaction with hydroxyl group at ordinary conditions such as a room temperature to 150°C and an ordinary pressure,

is not particularly limited. Herein, there is preferably employed a compound containing an acid anhydride group having a cyclic (unsaturated or saturated) group having a carbon number of 8-12, particularly, 8-10. By the use of such the compound, compatibility becomes excellent in a resin obtained.

As the acid anhydride, there can be employed an anhydride of the carboxylic acid described in the above-described I-1-1 (2) and, preferably, there are enumerated phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 4-methyl hexahydrophthalic anhydride, and trimellitic anhydride, etc.

As specific examples of the ethylenic unsaturated monomer (f) having an acid anhydride group to be employed herein, there are enumerated itaconic anhydride, maleic anhydride, and cytraconic anhydride, etc.

As specific examples of the monoalcohol (g) to be employed herein, there are enumerated methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, t-butanol, n-hexylalcohol, lauryl alcohol, methylcellosolve, ethylcellosolve, methoxypropanol, ethoxypropanol, fufuryl alcohol, dimethylaminoethanol, acetol, allyl alcohol, and propalgyl alcohol, etc.

I-1-3. <Ethylenic unsaturated monomer (a2) not having carboxylic group>

As specific examples of the ethylenic unsaturated monomer (a2) not having carboxylic group which is another monomer component to be employed for the copolymerization of the acrylic polycarboxylic acid

resin (A'), for example, there are enumerated styrene, α -methylstyrene, p-t-butylstyrene, (meth)acrylate (for example, methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, n-, i-, and t-butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate and lauryl(meth)acrylate, cyclohexyl(meth)acrylate, and isobonyl(meth)acrylate, etc.), Veova-9 and Veova-10 manufactured by Shell, AG.

In the case that styrene and a styrene derivative are employed as the ethylenic unsaturated monomer (a2) not having carboxylic groups, those are preferably employed in an amount of 5-40% by weight.

I-2. <Acrylic polycarboxylic acid resin (A'') having carboxylic groups and carboxylate groups>

As the acrylic polycarboxylic acid resin (A') to be employed for the curable resin composition of the present invention, the acrylic polycarboxylic acid resin (A'') having carboxylic groups and carboxylate groups is preferably employed, whereby, acid resistance is improved in a coating a composition obtained.

The acrylic polycarboxylic acid resin (A'') having carboxylic groups and carboxylate groups is obtained by allowing to react 5-50% by weight of the hydroxyalkyl(meth)acrylate composition having carboxylic groups (a') modified by a small amount of lactones and 5-50% by weight of the acrylic polyacid anhydride (a3) with 5-50% by weight of the monoalcohols (g).

As proportion of the monomer (a') which constructs the acrylic polycarboxylic acid resin (A'') having carboxylic groups and carboxylate groups, it is preferably 5-50% by weight, and more

preferably 10-40% by weight.

In the case that the monomer (a') is less than 5% by weight, a coating layer unpreferably becomes hard and, in the case of exceeding 50% by weight, water resistance unpreferably becomes worse.

Further, in the case that the (3₃) exceeds 50% by weight, unreacted anhydride groups are remained and, resulting in that a storage stability becomes unpreferably worse and, in the case of less than 5% by weight, the monoalcohols (g) are excessively remained, unpreferably resulting in that lack of curing is caused in curing.

The acrylic polyacid anhydride (a3) is obtained by allowing to copolymerize 15-40% by weight, and preferably 15-35% by weight of the ethylenic unsaturated monomer (f) having an acid anhydride group with 60-85% by weight, and preferably 65-85% by weight of the ethylenic unsaturated monomer (d1) not having an acid anhydride group.

In the case that the amount of the ethylenic unsaturated monomer (f) having an acid anhydride group is less than 15% by weight, curability becomes short and, in the case of exceeding 40% by weight, a coating layer becomes excessively brittle, resulting in that weatherability becomes short. As specific examples of ethylenic unsaturated monomer (f) having an acid anhydride group, there are enumerated ones already illustrated.

The ethylenic unsaturated monomer (d1) not having an acid anhydride group, if it does not adversely affect to the acid anhydride group, is not particularly limited, and there is preferred a monomer having a carbon number of 3-15, particularly, 3-12 and having one ethylenic unsaturated bond.

A mixture of at least two ethylenic unsaturated monomers can be

also employed as the ethylenic unsaturated monomer (d1) not having an acid anhydride group. Because, it is effective for elevating a compatibility of resins themselves. Specifically, the above-described monomers are enumerated as the ethylenic unsaturated monomer (a2) not having carboxylic group. Monomers having carboxylic group such as acrylic acid, methacrylic acid, itaconic acid, and maleic acid can be employed as the ethylenic unsaturated monomer (d1) not having an acid anhydride group. Of those, scratch resistance in a coating layer is particularly preferably elevated by the use of a long chain carboxylic acid monomer having a spacer portion of carbon number of 5-20 pieces or so between an ethylenic unsaturated group and carboxylic group such as an adduct thereof with ϵ -caprolactone (for example, Alonix M-5300).

For example, as the ethylenic unsaturated monomer (d1) not having an acid anhydride group, there can be also employed an ethylenic unsaturated monomer (d2) having carboxylic group obtained by half-esterification reaction of the ethylenic unsaturated monomer (d3) having hydroxyl group with a compound having an acid anhydride group in 1/0.5-1/1.0, preferably, 1/0.8-1/1.0 of a molar ratio of hydroxyl group with respect to the acid anhydride group. In the case that the molar ratio is not less than 1/0.5, viscosity becomes high and workability becomes worse. In the case of not more than 1/1.0, an excessive acid anhydride is remained, and water resistance becomes worse in a coating layer.

In the ethylenic unsaturated monomer (d3) having hydroxyl group to be employed herein, a carbon number is preferably 2-40, and more preferably 4-20. In the case that a chain length is too short, flexibility is lost in the vicinity of crosslinking points, resulting in that a

coating layer becomes too hard and, in the case that it is too long, a molecular weight becomes too large between crosslinking points.

In general, there is enumerated the ethylenic unsaturated monomer (d3) having hydroxyl group which has an organic chain shown by the above-described general formula (4) or an organic chain shown by the above-described general formula (6).

Specifically, there are enumerated 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl(meth)acrylate, 2-hydroxybutyl (meth)acrylate, 4-hydroxybutyl(meth)acrylate, 6-hydroxyhexyl (meth)acrylate, and a reaction product thereof with ϵ -caprolactone and, a compound which can be prepared by esterification of a (meth)acrylic acid with a largely excessive diol (for example, 1,4-butane diol, 1,6-hexane diol, a polyethylene glycol, and a polypropylene glycol).

Such the compounds are commercially supplied, for example, 4-hydroxybutyl acrylate "4-HBA" and 4-hydroxybutylmethacrylate "4-HBMA" manufactured by Mitsubishi Kasei, Ltd., etc., and "Placel FM1" and "Placel FA1" manufactured by Daicel Chemical Industries, Ltd., etc. As a propylene oxide-based monomer, there are "Blemmer PP-1000" and "Blemmer PP-800" manufactured by Nihon Yushi, Ltd., and as an ethylene oxide-based monomer, there is "Blemmer PE-90" manufactured by Nihon Yushi, Ltd. As specific examples of the compound having an acid anhydride group, there are enumerated already exemplified ones.

The half esterification reaction of the ethylenic unsaturated monomer (d3) having hydroxyl group with the compound having an acid anhydride group is conducted according to usual methods, and it is

conducted at a temperature of room temperature to 150°C.

Copolymerization of the ethylenic unsaturated monomer (f) having an acid anhydride group with the ethylenic unsaturated monomer (d1) not having an acid anhydride group is conducted, for example, by a publicly-known method such as a solution polymerization which includes a radical polymerization. For example, it can be conducted at a polymerization temperature of 100-200°C under an ordinary pressure or compressurization for a polymerization time of period of 3-8 hours.

As an initiator, there is preferably employed an azo-based or peroxide-based initiator. There can be also employed other additives such as a chain transfer agent.

In the acrylic polyacid anhydride (a3) obtained, a number average molecular weight is 500-8000, further, 800-6000, particularly preferably 1500-4000. In the case that the number average molecular weight exceeds 8000, there lower compatibility of resins themselves and an outer appearance. In the case that the number average molecular weight is less than 500, curability becomes insufficient in a coating composition. The acrylic polyacid anhydride (a3) obtained has at least two, preferably 2-15 pieces of acid anhydride groups on an average in one molecule. In the case that the acid anhydride groups are less than 2 pieces in one molecule, curability becomes insufficient in a coating composition. In the case of exceeding 15 pieces, a coating layer becomes hard and too brittle and, weatherability is short.

Subsequently, the acrylic polycarboxylic acid resin (A'') having carboxylic groups and carboxylate groups is prepared by allowing to react the hydroxyalkyl(meth)acrylate composition having carboxylic groups (a') modified by a small amount of lactones and the acrylic

polyacid anhydride (a3) with the monoalcohol (g) in an amount of molar ratio of the acid anhydride group with respect to hydroxyl group of 1/10-1/1, preferably 1/5-1/1, and more preferably 1/2.0-1/1. In the case of being less than 1/10, an excessive amount of the monoalcohol is remained, and there is caused lack of curing and, in the case of exceeding 1/1, unreacted acid anhydride groups are remained, and storage stability becomes worse.

The monoalcohol (g) to be employed in the present invention has preferably 1-12 pieces, particularly, 1-8 pieces of carbon numbers, because an alcohol evaporates to excellently reproduce the acid anhydride group by heating. As preferred specific examples of the monoalcohol to be employed, there are enumerated already exemplified ones. There are particularly preferred acetol, fulfuryl alcohol, allyl alcohol, propargyl alcohol, and methanol.

The acrylic polycarboxylic acid resin (A'') having carboxylic groups and carboxylate groups obtained has an acid value of 5-300 mgKOH/g, and preferably 50-250 mgKOH/g. In the case that the acid value is less than 5 mgKOH/g, curability becomes short and, in the case of exceeding 300 mgKOH/g, storage stability unpreferably becomes short.

The acrylic polycarboxylic acid resin (A'') component can be formulated with the curable resin composition in an amount of 10-70% by weight, preferably 15-50% by weight, and more preferably 20-45% by weight based on total solid components in the curable resin composition. In the case that formulating amount of the acrylic polycarboxylic acid resin (A'') component is less than 10% by weight, acid resistance lowers in a coating layer obtained and, in the case of exceeding 70% by weight, the coating layer becomes too hard.

I-3. <Acrylic polycarboxylic acid resin (bA') in which carboxylic groups are blocked>

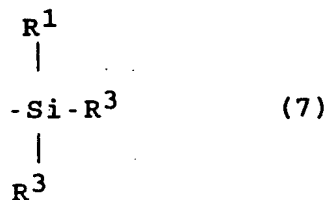
In the curable resin composition of the present invention, the acrylic polycarboxylic acid resin (bA') in which carboxylic groups are blocked can be employed in place of the acrylic polycarboxylic acid resin (A').

The acrylic polycarboxylic acid resin (bA') in which carboxylic groups are blocked to be employed in the present invention, if it is an acrylic polycarboxylic acid resin having carboxylic groups which are blocked by a blocking group which produces carboxylic group by heat and/or water (for example, moisture in atmosphere or water), can be employed without being particularly limited.

Such the blocked carboxylic group is shown by -COO-Z (Z is a blocked group derived from a blocking agent connected to hydroxyl group in carboxylic group).

As the Z, there can be preferably exemplified a silyl blocking group (K₁) or a vinyl ether blocking group (K₂) described below.

As the silyl blocking group (K₁), there can be exemplified a silyl blocking group represented by the following general formula (7).



In the above formula (7), R¹-R³ are independently an alkyl group or aryl group. As the alkyl group, there is enumerated a linear or branched lower alkyl group having a carbon atom number of 1-10 and, for example, there are particularly preferred methyl group, ethyl group,

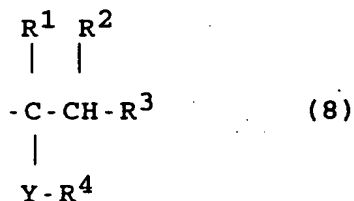
propyl group, butyl group, s-butyl group, t-butyl group, pentyl, and hexyl group. As the aryl group, there is enumerated phenyl group, naphthyl group, and indenyl group, etc. which may even have substituent groups, and phenyl group is particularly preferred.

As the silyl blocking group (K_1) represented by the general formula (7), there are enumerated trimethyl silyl group, diethyl methylsilyl group, ethyldimethyl silyl group, butyldimethyl silyl group, butylmethylethyl silyl group, phenyldimethyl silyl group, phenyldiethyl silyl group, diphenylmethyl silyl group, and diphenylethyl silyl group, etc. Particularly, in the R^1 - R^3 having smaller molecular weight, blocking group is readily unfastened, and preferably reactive.

As such blocking agents which produce such the silyl blocking group (K_1), a halogenated silane can be preferably employed. As halogens contained in the halogenated silane, there are enumerated chlorine atom or bromine atom, etc.

As specific blocking agents, for example, there are enumerated trimethyl silyl chloride, diethylmethyl silyl chloride, ethyldimethyl silyl chloride, butyldimethyl silyl bromide, and butylmethylethyl silyl bromide, etc.

As the vinylether blocking group (K_2), there is exemplified the following vinylether blocking group shown by formula (8) described below.



In the above formula (8), R^1 - R^3 are independently a hydrogen atom

or a hydrocarbon group having a carbon atom number of 1-18. R^4 is a hydrocarbon group having a carbon atom number of 1-18. Y is an oxygen atom or sulphur atom. Further, R^3 and R^4 may be mutually connected, and there may be formed a heterocyclic ring containing the Y as a hetero atom.

As the hydrocarbon atom in the above formula, there are enumerated an alkyl group, a cycloalkyl group, and an aryl group.

As the alkyl group, for example, there is particularly preferred a lower alkyl group having a carbon atom number of 1-8 such as methyl group, ethyl group, propyl group, butyl group, s-butyl group, t-butyl group, pentyl group, and hexyl group. As the cycloalkyl group, for example, there are enumerated cyclopentyl group and cyclohexyl group, etc. As the aryl group; there are included phenyl group, naphthyl group, and anthracene group, etc. which may have a substituent group, and phenyl group is particularly preferred.

Such the vinylether blocking group (K_2) can be formed by allowing to react an aliphatic vinylether or thioether, or a cyclic vinylether, or thioether with hydroxyl group in carboxylic group.

As the aliphatic vinylether, for example, there are enumerated methylvinylether, ethylvinylether, isopropyl vinylether, n-propylvinylether, isobutylvinylether, 2-ethylhexylvinylether, cyclohexylvinylether, or a vinylthioether corresponding thereto.

As the cyclic vinylether, for example, there are enumerated 2,3-dihydrofuran, 3,4-dihydrofuran, 2,3-dihydro-2H-pyran, 3,4-dihydro-2H-pyran, 3,4-dihydro-2-methoxy-2H-pyran, 3,4-dihydro-4,4'-dimethyl-2H-pyran-2-one, 3,4-dihydro-2-ethoxy-2H-pyran, and 3,4-dihydro-2H-pyran-2-sodium

carboxylate, etc.

As an epoxy group which is a second functional group, a nonalicyclic epoxy group and an alicyclic epoxy group are included.

As the nonalicyclic epoxy group, for example, there is exemplified a group in which an epoxy bond by oxygen atom is formed between carbon atoms in an alkyl group such as 1,2-epoxy group and 1,3-epoxy group. As the alicyclic epoxy group, for example, there is exemplified a group in which oxygen atom forms an epoxy bond between carbon atoms which are adjacent to a ring in a 5- or 6-membered ring (there is also included a hydrocarbon having a bridge). Of those, the nonalicyclic epoxy group is more preferably employed than the alicyclic epoxy group in a practical use.

In resins to be employed in the present invention, the above-described first and second functional groups may even exist in an identical resin, or in individual resins, respectively. Carboxylic group produces a secondary hydroxyl group in addition to the formation of an ester bond by reacting with an epoxy group.

Further, a blocked carboxylic group produces a free carboxylic group by disconnection of a blocked group, and the same reaction is caused as the above descriptions. In the curable resin composition of the present invention, a crosslinking (curing) reaction is caused and a resin is formed by a mutual reaction in such the functional groups.

I-4. <Polyepoxide (IX-B)>

Polyepoxide (IX-B) which is another constructing component in the curable resin composition of the present invention, if it is a compound having at least two pieces of epoxy groups on an average in

the molecule, preferably 2-10 pieces, and more preferably 3-8 pieces, is not particularly limited.

For example, there are enumerated glycidylethers (B_1) of a polyvalent alcohol and glycidylesters (B_2) of a polybasic acid.

As an example of the glycidylethers (B_1) of a polyvalent alcohol, there are enumerated glycerine triglycidylether, trimethylolpropane triglycidylether, pentaerythritol tetraglycidylether, and sorbitol hexaglycidylether, etc.

Further, as an example of the glycidylesters (B_2) of a polybasic acid, there is enumerated a glycidylester of hexahydrophthalic acid.

Polyepoxide (B') which is preferably employed in the present invention is an acrylic polyepoxide (B') which is obtained by copolymerization of 10-60% by weight, and preferably 15-50% by weight of an ethylenic unsaturated monomer (e) containing an epoxy group with 40-90% by weight, and preferably 50-80% by weight of an ethylenic unsaturated monomer (h) not containing an epoxy group.

In the case that the ethylenic unsaturated monomer (e) containing an epoxy group is not more than 10% by weight, curability is short and, in the case of more than 60% by weight, a resin becomes too hard and weatherability becomes short.

As the ethylenic unsaturated monomer (e) containing an epoxy group, for example, there are enumerated glycidyl(meth)acrylate, β -methylglycidyl(meth)acrylate, and 3,4-epoxycyclohexenyl(meth)acrylate, etc. In order to prepare a coating composition which is well-balanced between curability and storage stability, glycidyl(meth)acrylate is preferably employed.

As the ethylenic unsaturated monomer (h) not containing an epoxy

group, there are enumerated monomers described hereinabove as the ethylenic unsaturated monomer (d_1) not containing an acid anhydride group in order to prepare the polymer (A3) containing acid anhydride groups. Copolymerization can be also likewise conducted as described hereinabove.

In the acrylic polyepoxide (B') obtained, a number average molecular weight is 200-10000, preferably 500-8000, and more preferably 800-5000. In the case that the number average molecular weight is less than 200, curability lowers in a coating layer obtained and, in the case of exceeding 10000, solid component lowers in a coating. Further, an epoxy equivalent is 50-700, preferably 80-600, and more preferably 100-500. In the case that the epoxy equivalent is more than the maximum value, curability becomes unpreferably insufficient in a coating composition.

Further, in the case that it is less than the minimum value, a coating layer becomes unpreferably too hard and brittle.

Further, in order to prepare the ethylenic unsaturated monomer (d_1) not containing an acid anhydride group, the ethylenic unsaturated monomer (d_3) containing hydroxyl group can be employed as the ethylenic unsaturated monomer (h) not containing an epoxy group.

Particularly, in the case that the ethylenic unsaturated monomer (d_3) containing hydroxyl group is employed as the ethylenic unsaturated monomer (h) not containing an epoxy group, adhesion and a recoating property, etc. are elevated in a coating layer obtained. Still further, since an acrylic polyepoxide having hydroxy group and epoxy group obtained by employing the ethylenic unsaturated monomer (d_3) containing hydroxyl group as the ethylenic unsaturated monomer (h) not containing

an epoxy group, as described hereinafter, reacts and connects with an acrylic polycarboxylic acid (A') having carboxylic groups and carboxylate groups at both functional groups which are hydroxyl groups and carboxylic groups, a stronger coating layer can be obtained.

In the acrylic polyepoxide (B') obtained, a hydroxyl value is 5-300 mgKOH/g solid, preferably 10-200 mgKOH/g solid, and more preferably 15-150 mgKOH/g solid. In the case that the hydroxyl value exceeds 300 mgKOH/g solid, solid components lower in a coating and water resistance is insufficient in a cured coating layer and, in the case of less than 5 mgKOH/g solid, adhesion is poor.

A particularly preferred polyepoxide (B'') to be employed in the present invention is obtained by copolymerization of (i) 5-70% by weight of the ethylenic unsaturated monomer (d₃) containing hydroxyl group which has the organic chain shown by the general formula (4) or the organic chain shown by the general formula (6), (ii) 10-60% by weight of the ethylenic unsaturated monomer (e) containing an epoxy group, and optionally, (iii) 0-85% by weight of the ethylenic unsaturated monomer (d₄) not simultaneously containing hydroxyl group and epoxy group.

In the case, the polyepoxide (B'') having hydroxyl group and an epoxy group has preferably 2-12 pieces, more preferably 3-10 pieces of epoxy groups on an average and preferably 0.5-10 pieces, more preferably 1-8 pieces of hydroxyl group.

The polyepoxide (B'') component can be formulated in an amount of 10-80% by weight, preferably 20-70% by weight, and more preferably 30-65% by weight based on total solid of the curable resin composition.

In the case that the amount of the polyepoxide (B'') is less than 10% by weight, curability lowers in a coating layer obtained and, in the case of exceeding 80% by weight, yellowing resistance becomes worse.

I-5. <Anti oxidant (I-C)>

Usually, a hydrocarbon-based polymer suffers an oxidizing deterioration such as heat, light, oxygen, and mechanical shear force during preparation, processing, and using. It is known that the oxidizing deterioration depends upon an action of a self-oxidizing mechanism which is a radical continuous chain reaction.

An antioxidant for preventing the oxidizing deterioration of a polymer is classified into a radical continuous chain inhibitor (a primary antioxidant) such as a phenol-based antioxidant and an amine-based antioxidant, and a peroxide decomposing agent (a secondary antioxidant) such as a phosphorus-based antioxidant and a sulphur-based antioxidant.

The anti oxidant (IX-C) to be employed in the curable resin composition of the present invention is a phenol-based antioxidant (C_1), a phosphite-based antioxidant (C_2), and a thioether-based antioxidant (C_3). Any one of those may be even employed solely, and two or more kinds thereof are effectively employed in combination for an anti-yellowing property because of different anti-oxidizing mechanisms in the respective antioxidants.

The phenol-based antioxidant (C_1) is preferably employed in combination with the phosphite-based antioxidant (C_2) or the thioether-based antioxidant (C_3). By employing the phenol-based antioxidant (C_1) in combination with the phosphite-based antioxidant

(C₂), an anti-yellowing property is particularly preferably improved.

The phenol-based antioxidant (C₁) preferably has a highly massive and bulky substituent group such as, for example, t-butyl group at an ortho position of a phenol. Because, there is not apt to be caused a chain transferring of a free radical caught, and stability increases. More preferably, there is enumerated one having a bulky substituent group at both ortho positions.

As the phenol-based antioxidant (C₁), there are enumerated 2,6-di-t-butylphenol, 2,4-di-t-butylphenol, 2-t-butyl-4,6-di-methyl-phenol, 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-ethylphenol, 2,4,6-tri-t-butylphenol, 2,6-t-butyl-4-hydroxymethylphenol, 2,6-di-t-butyl-2-dimethylamino-p-cresol, n-octadecyl-3-(3',5'-di-t-butyl-4-hydroxyphenyl)propionate, styrenatephenol, 2,2'-methylene-bis-(4-methyl-6-t-butylphenol), 2,2'-methylene-bis-(6-cyclohexyl-4-methylphenol), 2,2'-butylidene-bis-(2-t-butyl-4-methylphenol), 4,4'-methylene-bis-(2,6-di-t-butylphenol), 1,6-hexanediol-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], tris(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate, tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane, 1,1,3-tris-(2-methyl-4-hydroxy-5-t-butylphenyl)butane, and 3,9-bis[1,1-di-methyl-2-{-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy}ethyl]-2,4,8,10-tetraoxaspyro[5,5]undecane, etc.

Preferred phenol-based antioxidant (C₁) are

2,6-di-t-butylphenol, 2-t-butyl-4,6-di-methyl-phenol,
2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-ethylphenol,
2,4,6-tri-t-butylphenol, styrenatephenol,
2,2'-methylene-bis-(4-methyl-6-t-butylphenol),
2,2'-methylene-bis-(6-cyclohexyl-4-methylphenol),
4,4'-methylene-bis-(2,6-di-t-butylphenol), and
tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propiona
te] methane, etc.

As commercially supplied phenol-based antioxidant (C_1), for example, there are enumerated Sumilizer (Sumilizer)BHT, Sumilizer -S, Sumilizer-BP-76, Sumilizer-MD-PS, Sumilizer-BP-101, Sumilizer-GA-80, Sumilizer-BBM-S, Sumilizer-WX-R, Sumilizer-MW, Sumilizer-GM, and Sumilizer-GS which are manufactured by Sumitomo Kagaku, Ltd., and Adekastab A0-20, Adekastab A0-30, Adekastab A0-40, Adekastab A0-50, Adekastab A0-60, Adekastab A0-75, Adekastab A0-80, Adekastab A0-330, Adekastab A0-616, Adekastab A0-635, Adekastab A0-658, Adekastab A0-15, Adekastab A0-18, Adekastab 328, and Adekastab 37, etc. which are manufactured by Asahi Denka, Ltd.

As the phosphite-based antioxidant (C_2), for example, tris(isodecyl)phosphite, tris(tridecyl)phosphite, phenyldiisodecyl phosphite, diphenylisooctyl phosphite, triphenyl phosphite, tris(nonylphenyl)phosphite, 4,4'-isopropylidene-diphenolalkyl phosphite, tris(mono- and di-mixed nonylphenyl)phosphite, tris(2,4-di-t-butylphenyl)phosphite, distearyl pentaerythritol diphosphite, di(2,4-di-t-butylphenyl)pentaerythritol diphosphite, di(nonylphenyl)pentaerythritol diphosphite, phenyl-bisphenol A pentaerythritol diphosphite,

tetratridecyl-4,4'-butylidenebis-(3-methyl-6-t-butylphenol)-di-phosphite, and hexatridecyl 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butanetriphosphite, etc.

Preferred phosphite-based antioxidant (C_2) are tris(isodecyl)phosphite, phenyldiisodecyl phosphite, diphenylisooctyl phosphite, triphenyl phosphite, distearyl-pentaerythritol diphosphite, di(nonylphenyl)pentaerythritol diphosphite, phenyl-bisphenol A pentaerythritol diphosphite, and tetratridecyl-4,4'-butylidenebis-(3-methyl-6-t-butylphenol)-di-phosphite, etc.

As commercially supplied phosphite-based antioxidant (C_2), for example, there are enumerated Sumilizer TMP, and Sumilizer TPP-R, Sumilizer P-16 which are manufactured by Sumitomo Kagaku, Ltd., and Adekastab PEP-2, Adekastab PEP-4C, Adekastab PEP-8, Adekastab PEP-8F, Adekastab PEP-8W, Adekastab PEP-11C, Adekastab PEP-24G, Adekastab PEP-36, Adekastab HP-10, Adekastab 2112, Adekastab 260, Adekastab P, Adekastab QL, Adekastab 522A, and Adekastab 329K, Adekastab 1178, Adekastab 1500, Adekastab C, Adekastab 135A, Adekastab 517, Adekastab 3010, and Adekastab TPP, etc. which are manufactured by Asahi Denka, Ltd.

As the thioether-based antioxidant (C_3), for example, there are enumerated dilauryl-3,3'-thiodipropionate, ditridecyl-3,3'-thiodipropionate, dimylstyryl-3,3'-thiodipropionate, distearyl-3,3'-thiodipropionate, bis(2-methyl-4-{3-n-alkylthiopropionyloxy}-5-t-butylphenyl)sulphi

de, pentaerythritol-tetrakis-(β -lauryl-thiopropionate), and 2-mercaptobenzimidazole, etc.

As commercially supplied thioether-based antioxidant (C_3), for example, there are enumerated Sumilizer TPL-R, Sumilizer TPM, Sumilizer TPS, Sumilizer TP-D, Sumilizer TL, and Sumilizer MB which are manufactured by Sumitomo Kagaku, Ltd., and Adekastab A0-23, Adekastab A0-412S, and Adekastab A0-503A, etc. which are manufactured by Asahi Denka, Ltd.

The antioxidant (IX-C) is formulated in a proportion of 0.1-10% by weight, preferably 0.5-8% by weight, and more preferably 1-7% by weight based on total solid components in the curable resin composition [A' + (IX-B) + (IX-C)]. In the case that the amount of the antioxidant is less than 0.1% by weight, yellowing is remarkably observed in baking and, in the case of exceeding 10% by weight, curability lowers in a coating layer.

II. <Curable resin composition>

II-1. <Formulation of the curable resin composition>

The curable resin composition of the present invention is obtained by formulating the acrylic polycarboxylic acid resin (A') and the polyepoxide (IX-B), or the acrylic polycarboxylic acid resin (A'), the polyepoxide (IX-B), and the antioxidant (IX-C).

Formulation of the acrylic polycarboxylic acid resin (A'), the polyepoxide (IX-B), and the antioxidant (IX-C) can be readily conducted in an amount and method well known by a skilled person in the art. Particularly, in the case of using an acrylic polycarboxylic acid resin

(A'') having carboxylic groups and carboxylate groups, and a polyepoxide (B') having hydroxyl group and an epoxy group as a polyepoxide, there can be obtained a curable resin composition having a high solid content which can provide a coating layer having an excellent acid resistance.

In the case, the formulation is conducted in a molar ratio of the carboxylic groups contained in the acrylic polycarboxylic acid resin (A'') with respect to the epoxy group contained in the polyepoxide (B') of 1/1.2-1/0.6, and preferably 1/1.0-1/0.8, and molar ratio of the carboxylate groups contained in the acrylic polycarboxylic acid resin (A'') with respect to the hydroxyl group contained in the polyepoxide (B') of 1/1.5-1/0.2, preferably 1/1.2-1/0.25, and more preferably 1/1-1/0.3.

In the case that the molar ratio of the carboxylic groups contained in the resin (A'') with respect to the epoxy group contained in the polyepoxide (B') is less than 1/1.2, a coating layer yellows and, in the case of exceeding 1/0.6, curability lowers in a resin composition obtained. In the case that the molar ratio of the carboxylate groups contained in the resin (A'') with respect to the hydroxyl group contained in the polyepoxide (B') is less than 1/1.5, water resistance lowers because of excessive hydroxyl groups and, in the case of exceeding 1/0.2, curability lowers in a resin composition obtained. The formulating amount can be calculated from a hydroxyl value, acid value, and epoxy equivalent of resins according to a calculating method well known by a skilled person in the art.

In thus-obtained curable resin composition of the present invention, a curing mechanism is as follows. First of all, the carboxylic group react with the carboxylate groups in the acrylic polycarboxylic

resin (A') or the resin (A'') by heating to form acid anhydride groups in a polymer, and a free monoalcohol is produced. The monoalcohol produced is removed out of a system by evaporation. The acid anhydride groups produced in a polymer form again carboxylic groups by forming crosslinking points through a reaction with the hydroxyl groups contained in the polyepoxide (IX-B). The carboxylic groups form crosslinking points by a reaction with the epoxy groups in the polyepoxide (IX-B). As described hereinabove, a high crosslinking density can be provided by an advance of a curing.

II-2. <Polyester polycarboxylic acid>

In addition to the above-described essential components, there can be optionally formulated a binder component such as a polyester polycarboxylic acid (IX-D) into the curable resin composition of the present invention. It is effective for elevating a solid content in a coating layer obtained.

The polyester polycarboxylic acid (IX-D) to be employed in the curable resin composition of the present invention is obtained by a half-esterification reaction of a polyester polyol (k) having at least three hydroxyl groups with an acid anhydride.

In the present invention, the polyester polyol (k) means a polyvalent alcohol having at least one ester bond chain, and preferably at least two ester bond chains.

The polyester polycarboxylic acid (IX-D) to be employed in the curable resin composition of the present invention has an acid value of 50-350 mgKOH/g solid, preferably 100-300 mgKOH/g solid, and more preferably 150-250 mgKOH/g solid, a number average molecular weight

of 400-3500, preferably 500-2500, and more preferably 700-2000, and weight average molecular weight/number average molecular weight of not more than 1.8, preferably not more than 1.5, and more preferably not more than 1.35.

In the case that the acid value exceeds 350 mgKOH/g solid, polymer viscosity becomes too high, resulting in that concentration of solid components lowers and, in the case that the acid value is less than 50 mgKOH/g solid, curability is short in a coating layer.

In the case that the molecular weight exceeds 3,500, polymer viscosity becomes too high, resulting in that handling becomes difficult and concentration of solid components lowers in a coating composition and, in the case that the molecular weight is less than 400, curability is short in a coating layer or water resistance lowers in a coating layer. In the case that the weight average molecular weight/number average molecular weight exceeds 1.8, water resistance lowers or weatherability lowers in a coating layer.

Further, the polyester polycarboxylic acid (IX-D) may even have a hydroxyl value of not more than 150 mgKOH/g solid, preferably 5-100 mgKOH/g solid, and more preferably 10-80 mgKOH/g solid, whereby, adhesion elevates in a coating layer obtained. In the case that the hydroxyl value exceeds 150 mgKOH/g solid, water resistance lowers in a coating layer.

Half-esterification can be conducted by same operations using the above-described acid anhydride for preparing the ethylenic unsaturated monomer having carboxylic group to be employed as the ethylenic unsaturated monomer (d_1) not having an acid anhydride group. However, the hydroxyl groups may be even remained without necessity

of changing all the hydroxyl groups in the polyester polyol (k) to carboxylic groups. The polyester polycarboxylic acid (D₁) having hydroxyl groups provides a coating layer having an excellent adhesion such as a recoating property compared to the polyester polycarboxylic acid (D₂) not having hydroxyl group.

Further, since the polyester polycarboxylic acid (D₃) having hydroxyl groups and carboxylic groups, as described hereinafter, can react and connect to both of the polyepoxide (B') and the acrylic polycarboxylic acid resin (A'), there can be obtained a tough coating layer.

There is preferred one having not less than 0.1 piece of hydroxyl groups on an average in the molecule.

In general, mol amount of acid anhydride groups with respect to mol amount of OH groups in the polyester polyol (k) is desirably controlled in 0.2-1.0 times and, particularly 0.5-0.9 times. In the case that the mol amount of acid anhydride groups with respect to mol amount of OH groups is less than 0.2, curability is short in a coating layer.

The polyester polyol (k) to be employed herein provides a polyester polycarboxylic acid (D) having at least two acid-functional groups in the molecule and the above-described characteristics by reacting with an acid anhydride.

In general, such the polyester polyol (k) is prepared by condensation of a low molecular weight polyvalent alcohol having at least three hydroxyl groups and a carbon number of 3-16 with a linear aliphatic dicarboxylic acid. By introducing a linear aliphatic group

into the low molecular weight polyvalent alcohol, flexibility is given in a coating layer obtained, whereby, impact resistance elevates.

As the low molecular weight polyvalent alcohol to be employed, there are enumerated trimethylol propane, trimethylol ethane, 1,2,4-butanetriol, ditrimethylol propane, pentaerythritol, dipentaerythritol, glycerine, and a mixture thereof.

As the dicarboxylic acid, there are enumerated a dibasic acid such as phthalic acid, isophthalic acid, terephthalic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, tetrahydrophthalic acid, hexahydrophthalic acid, maleic acid, fumaric acid, and a mixture thereof. Further, there can be employed an acid anhydride such as succinic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, hemic anhydride, trimellitic anhydride, methylcyclohexene tricarboxylic anhydride, pyromellitic anhydride, and a mixture thereof.

The polyester polyol (k) is synthesized by a usual esterification reaction. That is, it is polyesterized by a dehydrating condensation reaction of a polyvalent alcohol with a polybasic acid, an esterification of a polyvalent alcohol with an acid anhydride and then a dehydrating reaction with an alkyl component. By such the operations, an oligomer of a polyester polyol (k) having a relatively low molecular weight, and there is provided a coating composition having a high solid.

A particularly preferred polyester polyol (k) to be employed in the present invention is obtained by chain extending through addition of a lactone compound such as ϵ -caprolactone to a low molecular weight polyvalent alcohol. Since a molecular weight distribution becomes sharp, a coating composition becomes high-solid, and there is obtained a

coating layer having an excellent weatherability and water resistance.

As a low molecular weight polyvalent alcohol to be particularly preferably employed in the case, there are enumerated trimethylol propane, ditrimethylol propane, and pentaerythritol, etc.

The lactone compound to be employed in the present invention may be a cyclic compound which produces hydroxyl group at a terminal by ring-opening through reacting with a nucleophilic agent because of the presence of oxygen atom in the ring. A preferred lactone compound has a carbon number of 4-7. Because, it readily causes a ring-opening addition reaction.

As a specific example of the lactone to be preferably employed, already exemplified ones are enumerated, and there are preferably employed ϵ -caprolactone, δ -varelolactone, and γ -butyrolactone.

Chain extension can be conducted by the same conditions as in a usual ring opening addition reaction. For example, a polyester polyol (k) is obtained by allowing to react at 80-200°C within 5 hours in an appropriate solvent or the absence of a solvent, which is chain-extended by a low molecular weight polyvalent alcohol. A tin-based catalyst may be even employed.

In the case, a mol amount of the lactone compound is 0.2-10 times, preferably 0.25-5 times, and more preferably 0.3-3 times with respect to a mol amount of OH group in the low molecular weight polyvalent alcohol. In the case that the mol amount of the lactone compound with respect to a mol amount of OH group is less than 0.2 times, a resin becomes hard, and impact resistance lowers in a coating layer and, in the case of exceeding 10 times, hardness lowers in the coating layer.

The polyester polycarboxylic acid (IX-D) component can be formulated within 70% by weight, preferably 5-50% by weight, and more preferably 10-40% by weight based on total solid in the curable resin composition. In the case that amount of the polyester polycarboxylic acid (IX-D) is less than 5% by weight, solid concentration does not increase in a coating and, in the case of exceeding 70% by weight, weatherability lowers in a coating layer obtained.

II-3. <Silicone polymer (IX-L)>

In the curable resin composition of the present invention, there can be optionally formulated a binder component such as a silicone polymer (IX-L). It is effective for elevating a solid component concentration in a coating layer obtained.

The silicone polymer (IX-L) to be employed in the present invention is, for example, a silicone polymer having an epoxy group and/or an alkoxy group.

As the silicone polymer (L_1) having epoxy groups, for example, there is enumerated a "NUC silicone" series manufactured by Nihon Unicar, Ltd.

As the silicone polymer (L_2) having alkoxy groups, for example, there is enumerated "KC89-S", etc. manufactured by Shin-etsu Kagaku Kogyo, Ltd.

As the silicone polymer (L_3) having epoxy groups and alkoxy groups, for example, there are enumerated "MKC silicate MSEP 2" series manufactured by Mitsubishi Kagaku, Ltd., and a "NUC silicone" series manufactured by Nihon Unicar, Ltd.

A method for the preparation of such the silicone polymers is described in pages 29-30 of Abstracts in Organic Silicone Material Chemical Symposium in 1990. The epoxy group can exist at middle portions or terminals of a linear or cyclic hydrocarbon chain.

In the present invention, an epoxy equivalent represents g-number of a compound containing 1 g equivalent of an epoxy group, an alkoxy equivalent represents g-number of a compound containing 1 g equivalent of an alkoxy group, and a hydroxyl group equivalent represents g-number of a compound containing 1 g equivalent of hydroxyl group.

In the silicone polymer (IX-L), the epoxy equivalent is 100-1500, and the alkoxy equivalent is 50-1500. In the case that the epoxy equivalent is less than 100, storage stability becomes poor in a coating and, in the case of exceeding 1500, curability becomes poor. A range of the epoxy equivalent is preferably 140-1000, and more preferably 180-700. A range of the alkoxy equivalent is preferably 60-800, and more preferably 80-500.

Such the silicone polymer (L₃) component having epoxy groups and alkoxy groups can be formulated within 30% by weight based on the total solid weight of the curable resin composition, preferably 3-20% by weight, and more preferably 5-15% by weight.

In the case that an amount of the silicone polymer (L₃) component exceeds 30% by weight, storage stability becomes poor in a coating obtained.

In the present invention, a silicone polymer (L₄) having hydroxyl groups and carboxylic groups can be employed together with or in place of the silicone polymers (L₁, L₂, and L₃) having epoxy groups and/or alkoxy groups. The silicone polymer (L₄) having hydroxyl groups and

carboxylic groups is obtained by a half-esterification reaction of a silicone polymer having hydroxyl group with a compound having an acid anhydride group.

In the silicone polymer (L_4), a number average molecular weight is 500-6000, and preferably 1000-4500, a hydroxyl group value is 2-120 mgKOH/g solid, and preferably 10-80 mgKOH/g solid, and an acid value is 20-180 mgKOH/g solid, and preferably 35-150 mgKOH/g solid. In the case that the number average molecular weight and hydroxyl group value or acid value exceed maximum value of the ranges, it becomes difficult to prepare a coating having a sufficiently high solid content and, in the case of less than minimum value of the ranges, curability lowers in a coating.

The silicone polymer having hydroxyl groups is commercially supplied, for example, there are enumerated KR-2001 manufactured by Shin-etsu Silicone, Ltd., and NUC silicone series manufactured by Nihon Unicar, Ltd., etc.

The silicone polymer having hydroxyl groups has preferably 3-12 pieces of hydroxyl groups on an average in the molecule. In the case that the hydroxyl groups is less than 3 on an average, curability is short and, in the case of exceeding 12, viscosity becomes high, resulting in that it becomes difficult to increase solid content in the case of preparation of a coating composition.

The compound having an acid anhydride group, if it is a compound which can provide a carboxyl-functional property by reacting with hydroxyl group in usual reaction conditions such as a room temperature to 120°C and an ordinary pressure, is not particularly limited. By the

use of a compound having an acid anhydride group and having a saturated or unsaturated cyclic group of a carbon number of 8-12, compatibility with a resin becomes preferably excellent.

As the compound having an acid anhydride group, for example, there are enumerated hexahydrophthalic anhydride, phthalic anhydride, 4-methylhexahydrophthalic anhydride, tetrahydrophthalic anhydride, and trimellitic anhydride, etc.

Half-esterification reaction of the silicone polymer having hydroxyl group with the compound having an acid anhydride group is conducted according to usual methods, for example, at room temperature to 120°C for 30 minutes to 8 hours. In the case that the reaction is conducted for a long time of period exceeding 120°C, polyesterization reaction is caused and there is produced a silicone polyester (IX-L) having a high molecular weight. Since such the silicone polyester (IX-L) has a small amount of functional groups and high viscosity, it is not preferred to be employed in the present invention.

Such the silicone polymer (L_4) having hydroxyl groups and carboxylic groups can be formulated within 30% by weight based on the total solid weight of the curable resin composition, preferably 3-20% by weight, and more preferably 5-15% by weight. In the case that an amount of the silicone polymer (L_4) component exceeds 30% by weight, storage stability becomes poor in a coating obtained.

In the case that the silicone polymer (L_3) having epoxy groups and alkoxy groups is employed together with the silicone polymer (L_4) having hydroxyl groups and carboxylic groups, total amount is within 30% by weight based on the total solid weight of the curable resin

composition, preferably 3-20% by weight, and more preferably 5-15% by weight. In the case that an amount of the silicone polymers (L_3+L_4) component exceeds 30% by weight, storage stability becomes poor in a coating obtained.

II-4. <Catalyst for curing>

In addition to the above-described components, a catalyst for curing (IX-F) is employed in the curable resin composition of the present invention. For example, there may even contain a catalyst for curing (F_1) such as a quaternary ammonium salt to be usually employed for an esterification reaction of an acid with an epoxide. As specific examples of other catalyst for curing (F_2) to be employed in the curable resin composition of the present invention, there are enumerated benzyltriethyl ammonium chloride or bromide, tetrabutyl ammonium chloride or bromide, salysilate or glycolate, paratoluene sulphonate, nitrate, dibutyl phosphate, di-2-ethylhexyl phosphate, trimethylbenzyl ammonium dibutylphosphate, trimethylcetyl ammonium butylphosphate, octyl trimethyl ammonium dimethylphosphate, and dodecyltrimethyl ammonium diphenylphosphate, etc. These catalysts for curing may be even employed in mixing.

The catalyst for curing (IX-F) can be usually employed in 0.01-3.0% by weight based on the total solid weight of resin composition, preferably 0.1-1.5% by weight, and more preferably 0.4-1.2% by weight. In the case that an amount of the catalyst for curing (IX-F) is less than 0.01% by weight, curability lowers and, in the case of exceeding 3.0% by weight, storage stability lowers.

II-5. <Tin-based catalyst (IX-G)>

Further, as described in JP-A-02151651 and JP-A-02279713 Official Gazettes, a tin-based compound may be even employed together therewith. As the tin-based catalyst (IX-G), for example, there are enumerated dimethyltin bis(methylmaleate), dimethyltin bis(ethylmaleate), dimethyltinbis(butylmaleate), and dibutyltinbis(butylmaleate), etc.

The tin-based compound (IX-G) can be usually employed in 0.2-6% by weight based on the total solid weight of resin composition, preferably 0.3-4.0% by weight, and more preferably 0.4-3.0% by weight.

In the case that an amount of the tin-based compound (IX-G) to be employed is less than 0.2% by weight, storage stability lowers and, in the case of exceeding 6% by weight, weatherability lowers.

In the case that the catalyst (IX-F) for curing is employed together with the tin-based catalyst (IX-G), weight ratio of the catalyst (IX-F) for curing with respect to the tin-based catalyst (IX-G) is preferably adjusted to 1/4-1/0.2.

II-6. <Other additives (H)>

In order to elevate water resistance by elevating crosslinking, a blocked isocyanate may be even added in the curable resin composition of the present invention. Further, in order to improve weatherability in a coating layer, there may be even added an ultraviolet ray absorbent and a hindered amine photostabilizer, and an antioxidant, etc.

Still further, as a rheology controlling agent, a crosslinked resin particles (IX-E) may be added and, in order to control an outer appearance, a surface controlling agent may be even added.

In the case that the crosslinked resin particles (IX-E) are

employed, those are added in an amount of 0.01-10 parts by weight, preferably 0.1-5 parts by weight with respect to 100 parts by weight of solid resin of the curable resin composition of the present invention. In the case that the amount of the crosslinked resin particles (IX-E) exceed 10 parts by weight, outer appearance becomes worse and, it is less than 0.01 part by weight, a rheology controlling effect is not obtained.

Further, as a dilution agent in order to control a viscosity, there may be even added an alcohol-based solvent (for example, methanol, ethanol, propanol, and butanol, etc.), a hydrocarbon-based and ester-based solvent, etc.

Still further, the resin to be employed in the present invention has an acid group as a functional group. Accordingly, by neutralization using an amine, it can be also changed to a water-based composition containing water as a medium.

III. <Coating composition and preparation of a coating layer>

Method for the preparation of the coating composition of the present invention is not particularly limited and, there can be applied all methods which are well known in skilled person in the art.

The coating composition of the present invention can be coated by spray coating, brush coating, immersion coating, roll coating, and flow coating, etc. A substrate may be even optionally under-coated or middle-coated. As an under coating and a middle coating, publicly-known ones can be employed.

The coating composition of the present invention can be advantageously employed for, for example, woods, metals, glass, cloth,

plastics, and foams, etc., particularly, surface of the plastics and metals, for example, steels, aluminum, and an alloy thereof. In general, layer thickness changes depending upon desired uses. In many cases, it is useful in 0.5-3 mil.

After coating onto the substrate, coating layer is cured.

A cured coating layer having a high crosslinking degree is obtained at a curing temperature of 100-180°C, preferably 120-160°C. Curing time of period changes depending upon the curing temperature, etc., and it is appropriate in 120°C-160°C for 10-30 minutes.

By the curable resin composition in relation to the present invention, a high solid coating can be prepared, and a coating layer derived from the coating is excellent in acid resistance against an acid rain, abrasion resistance, yellowing resistance, and outer appearance, and it is an exceedingly useful composition.

Hereinafter, the present invention X is illustrated in detail.

As a polymerizable unsaturated monomer having carboxylic group to be employed in the present invention, for example, there are enumerated at least one selected from the group consisting of (meth)acrylic acid, itaconic acid, β -(meth)acryloyloxy ethylsuccinate, β -(meth)acryloyloxy ethylmaleate, β -(meth)acryloyloxy ethylphthalate, maleic acid, a monoalkylmaleate (a carbon number of 1-12 in the alkyl group), tetrahydrophthalic acid, and an anhydride thereof. Of those, acrylic acid and methacrylic acid are particularly preferred.

The present invention is comprised a composition obtained by allowing to react in a reaction molar ratio of a radical polymerizable

unsaturated monomer having carboxylic group of more than 1 in the case of preparing a lactone-modified radically polymerizable unsaturated monomer having carboxylic group by ring-opening polymerization of a lactone with the radically polymerizable unsaturated monomer having carboxylic group. In more detail, it is comprised a composition obtained by allowing to react the lactone with the polymerizable unsaturated monomer having carboxylic group at a temperature of approximately 80°C to approximately 140°C in an atmosphere containing oxygen under the presence of a catalyst less than 1000 ppm and an inhibitor less than 1000 ppm in order to prevent a polymerization of the polymerizable unsaturated monomer having carboxylic group.

Use amount of ϵ -caprolactone with respect to the radically polymerizable unsaturated monomer having carboxylic group is decided depending upon a molecular weight of a desired product, and it is particularly affected by an amount of the catalyst, a kind of a solvent, and an amount of the solvent. In order to reduce a lactone continuous chain, it is allowed to react with respect to not less than 0.3 mol and not more than 1 mol, preferably 0.35-1 mol, and more preferably 0.5-0.75 mol with respect to 1 mol of the radically polymerizable unsaturated monomer having carboxylic group. In the case that the reaction amount of the lactone is more than 1 mol, the lactone continuous chain becomes large and, in the case that it is employed, for example, as a raw material for a coating, although curing reactivity and flexibility become good, hardness and acid resistance lower in a cured article. Further, in the case of less than 0.35, abrasion resistance becomes worse.

As a catalyst to be employed in Nos. 15-16 of the present invention

X, for example, there are enumerated a Lewis acid such as aluminum chloride and stannous chloride, a Br nsted acid such as sulfuric acid, p-toluene sulphonate, benzene sulphonate, and a sulfonic acid-type ion-exchange resin, and there are preferred sulfuric acid, p-toluene sulphonate, and benzene sulphonate, since these are soluble in reaction liquid.

Use amount of the catalyst is preferably 0.1-50 parts by weight, and more preferably 0.1-20 parts by weight with respect to 100 parts by weight of the polymerizable unsaturated monomer having carboxylic group. In the case of employing the sulfonic acid-type ion-exchange resin, a large amount is required compared to sulfuric acid and p-toluene sulphonate.

As a catalyst to be employed in Nos. 15-16 of the present invention, although there have been conventionally employed aluminum chloride, stannous chloride, sulfuric acid, p-toluene sulphonate, benzene sulphonate, and the sulfonic acid-type ion-exchange resin, etc., even though intending to allow to add ϵ -caprolactone at a high temperature, since (meth)acrylic acid itself thermally-polymerizes, it is difficult to obtain a desired product, or there is observed discoloration of a product. At a low temperature, event though being capable of preventing a polymerization of acrylic acid itself, a ring-opening reaction rate of ϵ -caprolactone is very slow.

In the present invention, there is desirably employed a catalyst having a strong catalytic activity by which a reaction sufficiently proceeds at a low temperature such as 80-130°C and a small amount of the catalyst, and discoloration is low in a product obtained. From such a viewpoint, there are employed stannic chloride, monobutyltin

tris-2-ethylhexanoate, stannic octoate, and dibutyltin dilaurate, etc. Of those, discoloration can be decreased by the use of monobutyltin tris-2-ethylhexanoate, and concentration of a catalyst can be increased, and it is very excellent in a viewpoint of shortening of a reaction time of period.

Addition amount of the catalyst is 1-1000 ppm, and preferably 10-500 ppm.

By the use of the catalyst, there can become prepared a polyester unsaturated monomer composition modified by a small amount of lactones in which lactone continuous chains are decreased, and which is useful for preparing a polyester unsaturated monomer composition modified by a small amount of lactone. In contrast of a decrease of the lactone continuous chains, although there are remained unreacted polymerizable unsaturated monomers having carboxylic groups, since the unreacted polymerizable unsaturated monomers having carboxylic groups are often employed solely, if it is within 50 wt%, even mixed monomers can be often employed.

However, in the case that 1 mol of the lactone is added to 1 mol of the polymerizable unsaturated monomers having carboxylic groups, a reaction product is the compound represented by the above-described formula (1).

In a reaction composition, there are statistically distributed an unreacted substance having $n=0$ and polylactones having $n=1, 2, 3, 4, 5 \dots$. Herein, n is preferably not more than 2 and, an average value of n in the composition is not less than 0.3 and less than 1.0.

However, since it is difficult to industrially separate and refine those, in order to decrease products having not less than 2 continuous

chains, a feeding amount for reaction of the lactone such as ϵ -caprolactone is decreased to not more than 1 mol with respect to 1 mol of the polymerizable unsaturated monomers having carboxylic groups.

As the lactone monomers, there is preferred a lactone having 5, 6, 7, and 8-membered ring, for example, ϵ -caprolactone and/or varelolactone, etc. are enumerated. Further, in the case that ϵ -caprolactone is employed as the lactones, other cyclic lactones such as trimethylcaprolactone and varelolactone can be also partially employed in addition to ϵ -caprolactone.

The polyester unsaturated monomer composition modified by a small amount of lactones in relation to the present invention Nos. 15-16 is obtained by separating and removing unreacted (meth)acrylic acid from a reaction mass. As a method for separating and removing the unreacted (meth)acrylic acid, there are enumerated distilling separation, neutralizing separation (further, water washing may be also conducted) by a basic substance, and ion-exchanging separation, etc.

As solvents to be employed in the present invention, there are enumerated solvents which do not react with the catalysts, the lactones, and the polymerizable unsaturated monomers having carboxylic groups, and which include aromatic hydrocarbons such as benzene, toluene, and xylene. Further, it can be also prepared even in the absence of the solvents.

There is specifically illustrated below a method for the preparation of the polyester unsaturated monomer composition modified by a small amount of lactones of the present invention, in which the

reaction is conducted by collectively or continuously adding the lactones under the presence of 0.01-1% by weight, preferably 0.03-0.5% by weight of the catalysts and, optionally, a polymerization inhibitor such as hydroquinone, hydroquinone monomethylether, BHT, and phenothiazine at a reaction temperature of 40-150°C, and preferably 60-150°C based on 100 parts of the radically polymerizable unsaturated monomer having carboxylic group.

The solvents can be employed in concentration of, for example, 0-95% by weight (amount of solvents) in a reaction liquid.

In the polyester unsaturated monomer composition modified by a small amount of lactones prepared by the above-described method for the preparation of the present invention, residual amount of the lactones is 0-10% by weight (hereinafter, GPC area %), content of the polyester unsaturated monomer modified by a small amount of lactones is not less than 20% by weight and not more than 50% by weight, content of a di(meth)acrylate which is a by-product is not more than 2% by weight, content of other by-products prepared by Michaels addition, acrylic polymerization, esterification or other side reactions is not more than 10% by weight, content of the catalysts is less than 1000 ppm, and content of the polymerization inhibitors is not more than 1%.

The polyester unsaturated monomer composition modified by a small amount of lactones of the present invention can provide an acrylic polyol resin having an excellent reactivity with a crosslinking agent and rich flexibility by allowing to copolymerize with other radically polymerizable monomers. Further, it is useful for synthesizing a

flexible multifunctional (meth)acrylate containing urethane bonds by allowing to react with polyisocyanates. Products prepared by the present invention can be utilized, in addition to the above-mentioned coating, as a material for a photocurable resin, a reactive diluent for the photocurable resin, a flexibility agent for AS and ABS resins, an acrylic resin, a pressure sensitive adhesive, a flexible lens for a glass, an acrylic emulsion (particularly, a reaction type), a flexible reactive diluent for an unsaturated polyester resin instead of styrene, and a polymerizable polyurethane elastomer, etc.

As the other radically polymerizable monomers to be copolymerized with the polyester unsaturated monomer composition modified by a small amount of lactones of the present invention, there are enumerated an isocyanate group-contained unsaturated monomer, a polymerizable monomer containing an active hydrogen, and other polymerizable unsaturated monomers.

As the other polymerizable unsaturated monomers, the following ones are enumerated.

As (meth)acrylates, for example, there are enumerated alkyl or cycloalkyl(meth)acrylates having a carbon number of 1-20 such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, lauryl(meth)acrylate, cyclohexyl(meth)acrylate, isobonyl(meth)acrylate, adamantyl(meth)acrylate; and alkoxyalkyl(meth)acrylates having a carbon number of 2-8 such as methoxybutyl(meth)acrylate, methoxyethyl(meth)acrylate, and ethoxybutyl(meth)acrylate.

As monomers other than the (meth)acrylates, for example, there

are enumerated glycidyl(meth)acrylate; styrene, -methylstyrene, vinyltoluene, (meth)acrylonitrile, (meth)acrolein, butadiene, and isoprene, etc., and these can be employed in mixing.

As a polymerizable monomer containing an active hydrogen, there are enumerated (meth)acrylates containing hydroxyl group, and (meth)acrylates containing amino group, etc., and these can be employed in mixing.

As the (meth)acrylates containing hydroxyl group, there are enumerated hydroxyalkyl(meth)acrylates having a carbon number of 2-8 such as hydroxyethyl(meth)acrylate and hydroxypropyl(meth)acrylate, etc., and these can be employed in mixing.

As the (meth)acrylates containing amino group, for example, there are enumerated an aminoalkyl(meth)acrylate such as dimethylaminoethyl(meth)acrylate and diethylaminoethyl(meth)acrylate; and (meth)acrylamide, etc., and these can be employed in mixing.

As monomers containing isocyanate group, for example, there are enumerated isocyanateethyl(meth)acrylate, isocyanatepropyl(meth)acrylate, isocyanatebutyl(meth)acrylate, isocyanatehexyl(meth)acrylate, m-isopropenyl- α, α' -dimethylbenzyl isocyanate, and m-ethylenyl- α, α' -dimethylbenzyl isocyanate, etc., and there is enumerated an unsaturated compound in which a polyisocyanate compound such as hexamethylene diisocyanate is added to the polymerizable monomer containing an active hydrogen such as hydroxyethyl(meth)acrylate., and these can be employed in mixing.

The above-described radically polymerizable monomers can be also employed in mixing, and those are selected depending upon desired

physical properties.

The acrylic resin of the present invention is prepared by radical polymerization of the polyester unsaturated monomer modified by a small amount of lactones of the present invention and the above-described radically polymerizable monomers by publicly-known solution polymerization methods under the presence of radical polymerization initiators.

As the radical polymerization initiators, there can be employed a peroxide initiator such as benzoyl peroxide, t-butylhydroperoxide, cumylhydroperoxide, cumenhydroperoxide, t-butylperoxybenzoate, and t-butylperoxy-2-ethylhexanoate, and an azo-based initiator such as azobisisobutyronitrile and azobisdimethylvaleronitrile.

As solvents to be employed in the solution polymerization, for example, there are enumerated benzene, toluene, and xylene; an ester-based solvent such as butyl acetate, ethyl acetate, propyl acetate, and cellosolve acetate; an ether-based solvent such as dioxane and ethyleneglycol dibutylether; and a ketone-based solvent such as methylethylketone and methylisobutylketone, etc, and these can be employed solely or in mixing of two or more kinds.

As a reaction apparatus to be employed in the above-described polymerization, there are preferably employed a reaction vessel equipped with an agitator, a reflux condenser having a tube for drying and a twin-screw extruder.

Polymerization temperature and polymerization time of period depend upon a kind of the polyester unsaturated monomer modified by a small amount of lactones of the present invention and the above-described radically polymerizable monomers, feeding ratio, a

kind and amount of the catalysts, and the apparatus, those are not particularly limited, and are appropriately decided depending upon uses of a desired acrylic resin, for example, physical properties in, for example, a coating layer.

There is obtained a unitary compound of the polyester unsaturated monomer modified by a small amount of lactones or a mixture having a different addition mol amount of ϵ -caprolactone from a reaction solution containing thus-obtained polyester unsaturated monomer modified by a small amount of lactones.

Structure of the polyester unsaturated monomer modified by a small amount of lactones obtained can be identified and confirmed by measurement by an elementary analysis and a GPC analysis, of an acid value and double bond, etc.

According to the present invention, there can be prepared the polyester unsaturated monomer modified by a small amount of lactones having an identical radically polymerizable functional group to a radically polymerizable functional group contained in a radically polymerizable unsaturated monomer having carboxylic group in a short step and readily in an industrial fashion. Since the polyester unsaturated monomer modified by a small amount of lactones obtained has one radically polymerizable unsaturated group, and carboxylic group at a terminal, there can be expected a wide range utilization as a raw material or an intermediate for a thermosetting coating, an adhesive, a crosslinking agent, and an emulsion stabilizer, dispersant, and emulsifier for an emulsion, etc.

Further, in a composition in which the polyester unsaturated

monomer modified by a small amount of lactones is employed, tackiness can be removed by elevating Tg of the composition, and it is particularly useful in an electric material field, etc.

<Examples>

Hereinafter, although the present invention is illustrated by Examples, the present invention is not limited thereto.

It is to be noted that in the Examples, part and % are all based on the weight so far as particularly being defined.

I and II.

Example 1

A four-necked flask equipped with a tube for supplying air, a thermometer, a condenser, and an agitating device was charged with 2446 parts (18.8 mol) of 2-hydroxyethylmethacrylate (2-HEMA), 1610 parts (14.1 mol) of ϵ -caprolactone (ϵ -CL), 1.99 part of hydroquinone monomethylether (HQME) which is a polymerization inhibitor, and 0.199 part of stannous chloride (SnCl_2) which is a reaction catalyst, followed by allowing to react at 100°C for 23 hour while streaming air.

Reaction ratio of ϵ -caprolactone was 99.4%, and color hue of a reaction product was 20 (APHA).

An excellent acrylic polyol resin was obtained by copolymerization of a lactone-modified 2-hydroxyethylmethacrylate composition obtained with other monomers.

Example 2

A four-necked flask equipped with a tube for supplying air, a thermometer, a condenser, and an agitating device was charged with 2446 parts (18.8 mol) of 2-hydroxyethylmethacrylate (2-HEMA), 1610

parts (14.1 mol) of ϵ -caprolactone (ϵ -CL), 1.99 part of hydroquinone monomethylether (HQME) which is a polymerization inhibitor, and 0.795 part of monobutyltin tris-2-ethylhexanate which is a reaction catalyst, followed by allowing to react at 100°C for 6.5 hour while streaming air. Reaction ratio of ϵ -caprolactone was 99.3% (cf. Table 2), and color hue of a reaction product was 20 (APHA).

An excellent acrylic polyol resin was obtained by copolymerization of a lactone-modified 2-hydroxyethylmethacrylate composition obtained with other monomers. (cf. Example 5)

Example 3

A four-necked flask equipped with a tube for supplying air, a thermometer, a condenser, and an agitating device was charged with 2446 parts (18.8 mol) of 2-hydroxyethylmethacrylate (2-HEMA), 1073 parts (9.4 mol) of ϵ -caprolactone (ϵ -CL), 1.72 part of hydroquinone monomethylether (HQME) which is a polymerization inhibitor, and 0.690 part of monobutyltin tris-2-ethylhexanate which is a reaction catalyst, followed by allowing to react at 100°C for 7 hour while streaming air. Reaction ratio of ϵ -caprolactone was 99.6%, and color hue of a reaction product was 30 (APHA).

An excellent acrylic polyol resin was obtained by copolymerization of a lactone-modified 2-hydroxyethylmethacrylate composition obtained with other monomers (cf. Example 6).

Example 4

The same apparatus as in the Example 1 was charged with 504 parts (3.8 mol) of 2-hydroxyethylacrylate (2-HEA), 248 parts (2.2 mol) of ϵ -caprolactone, 0.368 part of hydroquinone monomethylether (HQME) which is a polymerization inhibitor, and 0.148 part of monobutyltin

tris-2-ethylhexanate, followed by allowing to react at 100°C for 7 hour while streaming air. Reaction ratio of ϵ -caprolactone was 99.3%, and color hue of a reaction product was 25 (APHA).

An excellent acrylic polyol resin was obtained by copolymerization of a composition obtained with other monomers (cf. Example 5).

Comparative Example 1

The same apparatus as in the Example 1 was charged with 2446 parts (18.8 mol) of 2-hydroxyethylmethacrylate, 2146 parts (18.8 mol) of ϵ -caprolactone, 2.25 part of hydroquinone monomethylether which is a polymerization inhibitor, and 0.900 part of monobutyltin tris-2-ethylhexanate which is a reaction catalyst, followed by allowing to react at 100°C for 8 hour while streaming air. Reaction ratio of ϵ -caprolactone was 99.0%, and color hue of a reaction product was 25 (APHA).

An excellent acrylic polyol resin was obtained by copolymerization of a lactone-modified 2-hydroxyethylmethacrylate composition obtained with other monomers (cf. Comparative Example 7).

Comparative Example 2

The same apparatus as in the Example 1 was charged with 799 parts (6.1 mol) of 2-hydroxyethylmethacrylate, 701 parts (6.1 mol) of ϵ -caprolactone, 0.735 part of hydroquinone monomethylether, and 0.147 part of tetrabutyl titanate (TBT), followed by allowing to react at 100°C for 64 hour while streaming air. Reaction ratio of ϵ -caprolactone was 99.6%, and color hue of a reaction product was 50 (APHA).

It was not able to obtain an acrylic polyol resin by the same copolymerization of a composition obtained with other monomers as in Example 5 because of an increased viscosity during reaction, and then

gelation.

Comparative Example 3

The same apparatus as in the Example 1 was charged with 1816 parts (14.0 mol) of 2-hydroxyethylmethacrylate, 3184 parts (27.9 mol) of ϵ -caprolactone, 2.50 part of hydroquinone monomethylether, and 1.00 part of monobutyltin tris-2-ethylhexanate, followed by allowing to react at 100°C for 8.5 hour while streaming air, and reaction ratio of ϵ -caprolactone was 99.2%, and color hue of a reaction product was 25 (APHA).

An excellent acrylic polyol resin was obtained by copolymerization of a lactone-modified 2-hydroxyethylmethacrylate composition obtained with other monomers (cf. Comparative Examples 9 and 10).

Comparative Example 4

The same apparatus as in the Example 1 was charged with 1816 parts (14.0 mol) of 2-hydroxyethylmethacrylate, 4776 parts (41.8 mol) of ϵ -caprolactone, 3.30 part of hydroquinone monomethylether, and 1.32 part of monobutyltin tris-2-ethylhexanate, followed by allowing to react at 100°C for 8 hour while streaming air, and reaction ratio of ϵ -caprolactone was 99.2%, and color hue of a reaction product was 25 (APHA).

An excellent acrylic polyol resin was obtained by copolymerization of a lactone-modified 2-hydroxyethylmethacrylate composition obtained with other monomers (cf. Comparative Example 11).

Comparative Example 5

The same apparatus as in the Example 1 was charged with 1816 parts (14.0 mol) of 2-hydroxyethylmethacrylate, 6364 parts (55.8 mol) of ϵ -caprolactone, 4.10 part of hydroquinone monomethylether, and 1.64

part of monobutyltin tris-2-ethylhexanate, followed by allowing to react at 100°C for 8.5 hour while streaming air, and reaction ratio of ϵ -caprolactone was 99.2%, and color hue of a reaction product was 30 (APHA).

It is to be noted that theoretical addition mol number of ϵ -caprolactone in the Examples and Comparative Examples is as follows.

Example 1: $n=0.75$, Example 2: $n=0.75$, Example 3: $n=0.50$, Example 4: $n=0.50$, Comparative Example 1: $n=1$, Comparative Example 2: $n=1$, Comparative Example 3: $n=2$, Comparative Example 4: $n=3$, Comparative Example 5: $n=4$

Product having $n=0.5$, product having $n=0.75$, product having $n=1$, product having $n=2$, and product having $n=3$ product having $n=4$ are shown as FM0.5, FM0.75, FM1, FM2, FM3, and FM4, respectively.

It is to be noted that FM shows a methacrylic acid series, and FA shows an acrylic acid series.

Table 1 and Figure 1 show an ϵ -caprolactone continuous chain distribution in the compositions obtained from GPC, and % is GPC area %.

[Table 1]

CLM numbers	0 (HEMA)	1	2	3	≥4*	>5	0~2 4	NV/Mn	≥2 (%)	≥3 (%)
Reference Example 1	27.0	36.7	24.3	9.5	2.5		100.0	1.27	36.3	12.0
Reference Example 2	26.3	36.3	24.5	9.6	3.3		100.0	1.24	37.4	12.9
Reference Example 3	38.2	38.3	17.7	4.8	1.0		100.0	1.21	23.5	5.8
Reference Example 4	35.1	39.5	19.0	5.2	1.1		100.0	1.22	25.4	6.4
Reference										
Comparative Example 1	19.9	28.3	26.9	15.4	9.5		100.0	1.30	51.8	24.9
Reference										
Comparative Example 3	6.2	16.7	25.9	23.2	15.7	12.3	87.7	1.28	77.1	51.2
Reference										
Comparative Example 4	3.1	8.1	17.0	21.9	20.7	29.3	70.7	1.28	88.8	71.8
Reference										
Comparative Example 5	1.4	3.9	9.9	16.4	19.6	48.9	51.1	1.26	94.8	84.9

* In the case that a peak by addition number of CLM of not less than 5 in small and cannot be separated from a peak having number 4, it is shown by 4. In the Comparative Example 2, it was not able to conduct a measurement because of gelation.

Tables 2 and 3 collectively show a reaction composition, reaction conditions, and characteristics of reaction products in the Examples 1-4 and Comparative Examples 1-5.

[Table 2]

	Reference Example			
	1	2	3	4
Reaction Composition				
2-HEMA (mol)	1	1	1	-
2-HEA	-	-	-	1
<i>t</i> -CL	0.75	0.75	0.5	0.5
HQME (ppm)	500	500	500	500
SnCl ₂ (ppm)	50	-	-	-
MBTTH (ppm)	-	200	200	200
TBT (ppm)	-	-	-	-
Reaction Conditions				
Reaction Temperature (°C)	100	100	100	100
Reaction Time of period (hrs)	23	6.5	7.0	7.0
Characteristics of Reaction Product				
<i>t</i> -CL reaction ratio (%)	99.4	99.3	99.6	99.3
Hydroxyl group value (mgKOH/g)	260	262	296	300
Acid value (mgKOH/g)	3.6	3.5	4.0	3.7
Color Hue (APHA)	20	20	30	25
Ethyleneglycol dimethacrylate or Ethyleneglycol diacrylate (%)	0.65	0.70	0.85	1.10

[* MBTTH: Monobutyltin tris-2-ethylhexanoate]

[Table 3]

	Reference Comparative Example				
	1	2	3	4	5
Reaction Composition					
2-HEMA (mol)	1	1	1	1	1
2-HEA	-	-	-	-	-
<i>t</i> -CL	1.0	1.0	2.0	3.0	4.0
HQME (ppm)	500	500	500	500	500
SnCl ₂ (ppm)	-	-	-	-	-
MBTTH (ppm) *	200	-	200	200	200
TBT (ppm)	-	100	-	-	-
Reaction Conditions					
Reaction Temperature (°C)	100	100	100	100	100
Reaction Time of period (hrs)	8.0	6.4	8.5	8.0	8.5
Characteristics of Reaction Product					
<i>t</i> -CL reaction ratio (%)	99.0	99.6	99.2	99.2	99.2
Hydroxyl group value (mgKOH/g)	223	225	153	116	94
Acid value (mgKOH/g)	3.7	3.7	2.7	2.0	1.7
Color Hue (APHA)	25	50	25	25	30
Ethyleneglycol dimethacrylate or Ethyleneglycol diacrylate (%)	0.35	3.96	0.28	0.20	0.15

Example 5

A four-necked flask equipped with a thermometer, a reflux condenser, a tube for supplying nitrogen gas, and an agitator was charged with 50 parts of butyl acetate, 50 parts of toluene, and 1.0 part of ditertiarybutyl peroxide (DTBPO), followed by elevating a temperature to 115°C. At a period having attained to 115°C, there were added dropwise 17.3 parts of styrene, 17.3 parts of butylmethacrylate, 17.3 parts of butylacrylate, 2.0 parts of methacrylic acid, 46 parts of the ϵ -caprolactone-modified 2-hydroxyethylmethacrylate composition synthesized in the Example 2, 0 part of 2-hydroxyethylmethacrylate, and 1.0 part of azobisisobutylnitrile over 3 hours, followed by continuing a reaction for 4 hours to obtain an excellent acrylic polyol resin transparent liquid (a-1). Table 4 and Table 5 show composition

of raw materials and characteristics of the resin solution, and Table 6 and Figure 2 show a relationship between feeding ratio of ξ -caprolactone/HEMA and a continuous chain distribution of ξ -caprolactone.

Example 6 and Comparative Examples 6-11

In the same apparatus and formulating conditions as in the Example 5, there were polymerized the ξ -caprolactone-modified acrylate compositions obtained in the Example 3 and Comparative Examples 1-4 and HEMA. Although it was able to obtain an excellent acrylic polyol resin transparent liquid from the monomers obtained in the Example 3 and Comparative Examples 3 and 4, in the case of the monomer obtained in the Comparative Example 2, since a reaction liquid caused a viscosity increase and gelation during polymerization, it was not able to obtain a resin solution.

Table 4 and Table 5 show composition of raw materials and characteristics of the resin solution in the respective Examples and Comparative Examples, and Table 6 and Figure 2 show a relationship between feeding ratio of ξ -caprolactone/HEMA and a continuous chain distribution of ξ -caprolactone.

[Table 4]

	Reference Example		Reference Comparative Example					
	5	6	6	7	8	9	10	11
Raw Material fed								
Butyl acetate	50	50	50	50	50	50	50	50
Toluene	50	50	50	50	50	50	50	50
DTBPO	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Styrene	17.3	19	23.3	15	17	7.0	15.8	16.3
Methyl methacrylate	17.3	19	23.3	15	17	7.0	15.8	16.3
Butyl methacrylate	17.3	19	23.3	15	17	7.0	15.8	16.3
Methacrylic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
<i>t</i> -caprolactone-modified acrylic monomer								
	Reference Example	Example	HEMA	Reference Comparative Example				
	2	3	used	1	1	3	3	4
	46	41	0	53.3	53.3	77	35.6	29.2
HEMA	0	0	28	0	9.1	0	15	20
AIBN	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

[Table 5]

	Reference Example		Reference Comparative Example					
	5	6	6	7	8	9	10	11
Acrylic poyol resin solution	a-1	a-2	RA-1	RA-2	RA-3	RA-4	RA-5	RA-6
Characteristics of Acrylic poyol resin solution								
Solid content (%)	50.1	51.1	50.0	50.0	50.6	50.5	50.3	51.1
Viscosity (cp 25°C)	650	1210	550	560	800	750	680	1120
Color hue (APHA)	35	35	30	30	30	30	35	35
(based on solid) Acid value (mgKOH/g)	15.8	16.5	16.2	16.3	16.2	16.2	15.8	16.5
(based on solid) Hydroxyl group value (mgKOH/g)	120	123	120	118	118	121	120	120
Tg (°C)	6	10	22	0	5	-19	1	2

[Table 6]

		ϵ -caprolactone continuous chain Distribution ratio (%)						ratio (%)
Continuous chain number→		0	1	2	3	4	≥5	≥2
Reference Example								
5	FM0.75	26.3	36.3	24.5	9.6	3.3	0.0	37.4
6	FM0.5	38.3	38.3	17.7	4.8	1.0	0.0	23.5
Reference Comparative Example								
6	HBMA	100.0						
7	FM1	19.9	28.3	26.8	15.4	9.5	0.0	51.8
8	FM1+HEMA	31.6	24.2	22.9	13.2	8.1	0.0	44.2
9	FM2	6.2	16.7	25.9	23.2	15.7	12.3	77.1
10	FM2+HEMA	34.0	11.8	18.2	16.3	11.0	8.7	54.2
11	FM3+HEMA	42.5	4.8	10.1	13.0	12.3	17.4	52.7

* the above-described FM-Number shows the feeding ratio of ϵ -caprolactone/HEMA.

In HEMA, the continuous chain distribution of ϵ -caprolactone is counted as 0.

In the polymerization of the acrylic polyol resins, OHV was set up at 120 and Tg was set up at 0-10°C in the Examples 5 and 6 and Comparative Examples 7, 8, 9, and 10. As a result, it is confirmed that a proportion of a 1 mol adduct (n=1) of ϵ -caprolactone is high in the Examples 5 and 6, and there becomes low a proportion of adducts in which 2 or more continuous chains of ϵ -caprolactone are added, and there lowers hardness in a melamine-cured product from the acrylic polyol resin.

In the case of employing a coating having a low proportion of the adducts in which 2 or more continuous chains of ϵ -caprolactone are added, for example, as a top-coating material for cars, there can be obtained a coating layer which is well-balanced among a hardness of a coating layer, a finishing outer appearance, weatherability, acid resistance, staining resistance, gloss, flexibility, and abrasion resistance.

Example III.

1. Preparation of a clear coating

A clear coating (series C) was prepared based on the formulation shown in Table III-7 described hereinafter.

A comparative clear coating (series SC) was prepared based on the formulation shown in Table III-7 described hereinafter.

2. Preparation of a solid color coating

Preparation of a solid color coating was conducted by adding titanium oxide to a mixture of a raw resin to be formulated with a melamine resin and dispersing by a motor mill (manufactured by Aiger Japan) for 30 minutes, and adding residual components to be formulated. A solid color coating (series S) was prepared based on the formulation shown in Table III-8 described hereinafter. A comparative solid color coating (series SR) was prepared based on the formulation shown in Table III-8 described hereinafter.

Evaluation of properties of a coating

1. Preparation of test pieces

A test piece molded from a polyolefin-based resin (X50 manufactured by Mitsui Kagaku) which is a body to be coated was washed by isopropylalcohol, and washed by a petroleum benzine.

2. Coating to a test piece

(1) in the case of a clear coating

A primer (Primax No. 1500 manufactured by Nihon Yushi) was coated in 15 m on the test piece and dried, and Primax No. 5500 (manufactured by Nihon Yushi) was coated as a base coat coating.

Subsequently, a clear coating prepared as hereinabove was diluted by a mixed thinner of xylene with Solvesso 100 as adjusted to 16 seconds in Ford cup No. 4, followed by coating the clear coating onto the test piece in wet-on-wet by air-spraying so that a dried coating layer becomes $30\mu\text{m}$ in the clear coating. After having placed for 10 minutes at a room temperature, it was dried by heating at 120°C for 30 minutes and 100°C for 30 minutes, and properties of the coating layer were measured after 24 hours. It is to be noted that a test in the case of coating a clear coating without using a primer is as follows. A base coat coating X was prepared as described below, and diluted by a thinner of toluene/ethyl acetate (weight ratio of 60/40) as adjusted to 13 seconds in Ford cup No. 4, followed by air-spraying so that a dried coating layer becomes $15\mu\text{m}$. Subsequently, a clear coating prepared as hereinabove was diluted by a mixed thinner of xylene with Solvesso 100 as adjusted to 16 seconds in Ford cup No. 4, followed by coating the clear coating onto the test piece in wet-on-wet by air-spraying so that a dried coating layer becomes $30\mu\text{m}$ in the clear coating. After having placed for 10 minutes at a room temperature, it was dried by heating at 120°C for 30 minutes and 100°C for 30 minutes, and properties of the coating layer were measured after 24 hours.

<Preparation of a base coat coating X>

- (a) Preparation of a grafted chlorinated polyolefin oligomer X having primary hydroxyl groups

A four-necked flask equipped with an agitating device, a thermometer, a tube for supplying an inert gas, a dropping funnel, and a reflux device was charged with 494 parts of toluene and 250 parts

of Hardlene 14ML (a chlorinated polyolefin manufactured by Toyo Kasei: chlorine content of 26%), followed by temperature elevating to 100°C while agitating. Subsequently, there was added dropwise a mixture composed of 142 parts of Placel FM-3, 104 parts of isobonylmethacrylate, 6 parts of benzoylperoxide, and 4 parts of azobisisobutyronitrile over 3 hours, and reaction was further continued for 6 hours to obtain a grafted chlorinated polyolefin oligomer X.

(b) Preparation of a base coat coating X

Formulation was conducted as follows.

	<u>Part</u>
Oligomer X	249
Super Bekkamine L-121-60	50
P-198	9
Butyl acetate	15
Xylene	15
Tinuvin 384	3
Tinuvin 123	1.5
Aluminum paste	15
<u>Modaflow</u>	<u>0.45</u>

(2) in the case of a solid color coating

A primer was coated as being adjusted to the thickness of 15 μ m as a dried coating layer on the test piece and dried, followed by diluting a solid color coating prepared as hereinabove by a mixed thinner of xylene with butyl acetate as being adjusted to 14 seconds in Ford cup No. 4, and followed by coating the clear coating onto the test piece by air spraying so that there becomes 30 μ m a dried coating layer in

the solid color coating. After having placed for 10 minutes at a room temperature, it was dried by heating at 120℃ for 30 minutes and 100℃ for 30 minutes, and properties of the coating layer were measured after 24 hours.

2. Evaluation method of properties

(1) Water resistance test

A molded article coated was partially immersed in warm water at 50℃ for 10 days. After having taken out, there was observed the presence or absence of adhesion and a blister.

Herein, test pieces of many peeling or blisters were evaluated as x, test pieces of no peeling or slight blisters were evaluated as , and test pieces of no causing peeling and blisters were evaluated as O.

(2) Gloss retention test

There was conducted an accelerating weatherability test by Sunshine-weatherometer (manufactured by Suga Shikenki), and there was measured a retention ratio (%) of a 60 -mirror surface glossiness after 1000 hours according to JIS K5400 (1979), and there was conducted an adhesion test according to JIS K5400 (1976) 6.15. Test pieces having the gloss retention ratio of not less than 80% and excellent adhesion were evaluated as , test pieces having the gloss retention ratio of not less than 70 and less than 80% and excellent adhesion were evaluated as , and test pieces having the gloss retention ratio of less than 70% and peeling in adhesion test were evaluated as x.

(3) Gasoline resistance

A molded article coated was partially immersed in a regular gasoline (Nisseki Silver gasoline manufactured by Nihon Sekiyu) at

20°C. After having being taken out, a swelling property was visually evaluated. Test pieces showing remarkable swelling were evaluated as x, test pieces showing slight swelling were evaluated as , and test pieces not showing swelling so much were evaluated as O.

(4) Acid resistance test

0.2 ml of 5%-sulfuric acid aqueous solution was dropped on a coating layer, followed by drying at 40°C for 30 minutes and visually observing a condition of the coating layer. Test pieces showing a mark were evaluated as x, test pieces slightly showing a mark were evaluated as , and test pieces not showing a mark were evaluated as O.

(5) Solid content in a coating

In a coating having a lower solid content, it is more difficult to prepare a thick coating layer. In the clear coating and solid color coating, a coating having not more than 30% of solid content was evaluated x, a coating having more than 30% and not more than 35% was evaluated as , a coating having not less than 35% and not more than 40% were evaluated as O, and a coating exceeding 40% were evaluated as ©.

Data of properties are collectively shown in Tables III-7 to III-8.

Table 8

Clear coating	Example				Comparative Example					
	C1	C2	C3	C4	SC-1	SC-2	SC-3	SC-4	SC-5	SC-6
Formulation										
A-1	100	100								
A-2			100	100						
RA-1					100					
RA-2						100				
RA-3							100			
RA-4								100		
RA-5									100	
RA-6										100
Superbekkamine L-121-60 (Dainippon Ink Kagaku Kogyo)	28	28	28	28	28	28	28	28	28	28
Tinuvin 384 (Ciba Geigy)	2	2	2	2	2	2	2	2	2	2
Sanol LS292 (Ciba Geigy)	1	1	1	1	1	1	1	1	1	1
Ajitol XL122 (Hoechst)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
P-198* (Dainippon Ink Kagaku Kogyo)	4	4	4	4	4	4	4	4	4	4
Xylol	24	24	24	24	24	24	24	24	24	24
Sonolebetts 100 (Exon)	40	70	70	100	70	70	70	70	70	70

Table 8 (continued)

Properties	C-1	C-2	C-3	C-4	SC-1	SC-2	SC-3	SC-4	SC-5	SC-6
Glass transition temperature (°C)	-10	-13	-7	-5	-3	-15	-10	-35	-10	-13
Weight average molecular weight	13000	12500	13500	14000	12000	12500	12500	13000	13500	12500
Number average molecular weight	8500	8500	8500	8500	8000	8300	8200	8200	8500	8200
Mw/Mn	1.53	1.47	1.59	1.65	1.50	1.51	1.52	1.59	1.59	1.52
Amount of functional group (mol/Kg resin)	1.0	1.1	1.7	1.9	1.1	1.1	1.2	1.1	1.1	1.2
Type* of melamine resin	B	B	B	B	B	B	B	B	B	B
Resin/melamine resin	79/21	←	←	←	←	←	←	←	←	←
Total acid value (mgKOH/g)	27	←	←	←	←	←	←	←	←	←
Characteristics										
120°C, 30 minutes										
Solid content in a coating	◎	○	○	△	△	○	○	○	○	○
Water resistance	○	○	○	○	○	○	○	△	△	△
Gloss	○	○	○	○	○	○	○	○	○	△
Gasoline resistance	○	○	○	◎	○	○	○	△	△	△
Acid resistance	○	○	○	△	◎	△	△	×	×	×
Abrasion resistance	○	○	○	○	×	○	○	○	○	◎
100°C, 30 minutes										
Solid content in a coating	◎	○	○	△	△	○	○	○	○	○
Water resistance	○	○	○	○	○	△	△	△	△	×
Gloss	○	○	○	○	○	○	○	△	△	△
Gasoline resistance	○	○	○	○	○	○	○	△	△	△
Acid resistance	○	○	○	○	◎	△	△	△	×	×
Abrasion resistance	○	○	○	○	×	○	○	○	○	◎

Note) P-198 is a mixed phosphate (manufactured by Dainippon Ink Kagaku Kogyo) composed of monobutyl phosphate and dibutyl phosphate.

Note) "A" in a type of a melamine resin means an imino type melamine resin. "B" in a type of a melamine resin means a methylol type melamine resin.

Mn: Number average molecular weight

Mw: Weight average molecular weight (hereinafter, the same also in Table 9)

Table 9

Solid color coating	S1	S2	S3	S4	RS-1	RS-2	RS-3	RS-4	RS-5	RS-6
Formulation										
A-1	166	166								
A-2			166	166						
RA-1					166					
RA-2						166				
RA-3							166			
RA-4								166		
RA-5									166	
RA-6										166
Superbekkamine	66	66	66	66	66	66	66	66	66	66
L-121-60										
P-198	6	6	6	6	6	6	6	6	6	6
Butyl acetate	120	160	160	180						
Xylene	160	200	200	200	200	←	←	←	←	←
Tinuvin 384	4	4	4	4	4	←	←	←	←	←
Sanol LS292	2	2	2	2	2	←	←	←	←	←
CR95	100	←	←	←	←	←	←	←	←	←
Modaflow (Monsant)	0.6	←	←	←	←	←	←	←	←	←

Table 9 (continued)

Properties	S-1	S-2	S-3	S-4	RS-1	RS-2	RS-3	RS-4	RS-5	RS-6
Glass transition temperature (°C)	-10	-13	-7	-5	-3	-15	-10	-35	-10	-13
Weight average molecular weight	13000	12500	13500	14000	12000	12500	12500	13000	13500	12500
Number average molecular weight	8500	8500	8500	8500	8000	8300	8200	8200	8500	8200
M _w /M _n	1.53	1.47	1.59	1.65	1.50	1.51	1.52	1.59	1.59	1.52
Amount of functional group (mol/Kg resin)	1.0	1.1	1.7	1.9	1.1	1.1	1.2	1.1	1.1	1.2
Type of melamine resin	B	B	B	B	B	B	B	B	B	B
Resin/melamine resin	70/30	←	←	←	←	←	←	←	←	←
Total acid value	23	←	←	←	←	←	←	←	←	←
Characteristics										
120°C, 30 minutes										
Solid content in a coating	◎	○	○	△	△	○	○	○	○	○
Water resistance	○	○	○	○	○	○	○	○	△	△
Gloss	○	○	○	○	○	○	○	○	○	△
Gasoline resistance	○	○	○	○	○	○	○	△	△	△
Acid resistance	○	○	○	△	○	△	△	×	×	×
Abrasion resistance	○	○	○	○	×	○	○	○	○	◎
100°C, 30 minutes										
Solid content in a coating	○	○	○	△	△	○	○	○	○	○
Water resistance	○	○	○	○	○	○	○	○	△	×
Gloss	○	○	○	○	○	○	○	△	△	△
Gasoline resistance	○	○	○	○	○	○	○	△	△	△
Acid resistance	○	○	○	○	○	△	△	△	×	×
Abrasion resistance	○	○	○	○	×	○	○	○	○	◎

By the Examples and Comparative Examples, it is clear that there can be prepared a coating layer well-balanced among hardness of the coating layer, outer appearance in finishing, weatherability, acid resistance, staining resistance, glossiness, and abrasion resistance in the case of employing products having a low proportion of two or more continuous chains of ϵ -caprolactone as a material for a top coating in cars.

Example IV.

In the hydroxyalkyl (meth)acrylate composition modified by a small amount of lactones obtained in the Example I, the composition obtained in the Example 2 is designated as (a-1), the composition obtained in the Example 3 is designated as (a-2), and the composition obtained in the Example 4 is designated as (a-3).

In the lactone-modified hydroxyalkyl (meth)acrylate composition obtained in the Comparative Examples of the Example I, the composition obtained in the Comparative Example 1 is designated as (a-1'), the composition obtained in the Comparative Example 3 is designated as (a-2'), the composition obtained in the Comparative Example 4 is designated as (a-3'), and the composition obtained in the Comparative Example 5 is designated as (a-4').

<Production of an acrylic polyol resin (A) solution>

Production Example IV-1

A four-necked flask equipped with a thermometer, an agitator, a reflux condenser, an tube for supplying nitrogen gas was charged with 30 parts of ethyleneglycol monobutylether, followed by elevating

a temperature to 120°C and maintaining.

In the flask, there was added dropwise a mixed solution of 31 parts of styrene, 21 parts of methylmethacrylate, 19 parts of 2-ethylhexyl methacrylate, 15 parts of the composition (a-1), 10 parts of hydroxyethylmethacrylate, 4 parts of acrylic acid, and 10 parts of 2,2'-azobisisobutyronitrile which is a polymerization initiator over 3 hours. After that, aging was conducted at 120°C for 1 hour and, subsequently, there was added dropwise a mixed liquid of 1 part of 2,2'-azobisisobutyronitrile which is an additional polymerization catalyst and 10 parts of ethyleneglycol monobutylether over 1 hour, aging was further conducted for 3 hours to obtain an acrylic polyol resin (A-1) solution having a solid content of approximately 71%.

In the resin (A-1) obtained, an acid value was 30, a weight average molecular weight (by GPC, hereinafter, the same) was approximately 9,500, and a glass transition temperature was 45°C.

Production Examples IV-2 to IV-3

The same procedures were conducted as in the Production Example IV-1, except that the composition (a-1) to be added dropwise was changed to the composition (a-2) or the composition (a-3) to obtain an acrylic polyol resin (A-2) solution or (A-3) solution.

Production Examples IV-4 to IV-7 (for references)

The same procedures were conducted as in the Production Example IV-1, except that the composition (a-1) to be added dropwise was changed to 2-hydroxyethylmethacrylate (HEMA) or the (a-1')-(a-4') in the Reference Comparative Examples to obtain acrylic polyol resin (A-1')-(A-4') solutions for references.

Production Example IV-8

Production Example of other acrylic resin (A#) solution

A four-necked flask equipped with a thermometer, an agitator, a reflux condenser, an tube for supplying nitrogen gas was charged with 30 parts of ethyleneglycol monobutylether, followed by elevating a temperature to 90°C and maintaining.

Into the flask, there was added dropwise a mixed solution of 35 parts of n-butylacrylate, 30 parts of 2-ethylhexyl methacrylate, 30 parts of N-n-butoxymethylmethacrylic amide, and 5 parts of acrylic acid, and 6 parts of benzoyl peroxide which is a polymerization initiator over 3 hours. After that, aging was conducted at 90°C for 5 hour to obtain an acrylic resin (A#) solution having a solid content of approximately 77%. In the acrylic resin (A#) obtained, an acid value was 39, a weight average molecular weight was approximately 10,000, and a glass transition temperature was -21°C.

Table IV-7 shows formulation ratio in the Production Examples IV-1 to IV-7 and physical properties of the resins obtained.

Table IV-8 shows formulation ratio in the Production Example IV-8 and physical properties of the resins obtained.

It is to be noted that the physical properties were measured according to the following methods.

Acid value in the resins: Sample was dissolved in a mixed solution of ethanol and toluene, and it was measured by a neutralizing titration of 0.1N solution of potassium hydroxide-ethanol using phenolphthalein as an indicator.

Weight average molecular weight: It was measured according to JIS K0124-83. Using TSK GEL G4000+G3000+G2500+G2000 (manufactured by Toyo Soda, Ltd.) as a column for separation, a measurement was conducted

at 40°C and a flow rate of 1.0 mm/minute, and it was calculated by a calibration curve prepared by a chromatogram obtained by an RI refractometer and a standard Polystyrene using tetrahydrofran for GPC as an eluate.

Glass transition temperature (T_g point): Using a differential scanning calorimeter DSC-50Q (Shimadzu Seisakusyo, Ltd.), it was measured from thermal spectra obtained in temperature elevation rate of 5°C/minute.

In the following Tables, IV is omitted.

Production No.	1	2	3	4	5	6	7
Mixed solution added dropwise							
Acrylic poyol resin	A-1	A-2	A-3	A-4	A-5	A-6	A-7
2-ethylhexylmethacrylate	19	←	←	←	←	←	←
Lactone-modified methacrylate	a-1:15	a-2:15	a-3:15	—	a-1':15	a-2':15	a-3':15
2-hydroxyethylmethacrylate	10	←	←	25	←	←	←
Acrylic acid	4	←	←	←	←	←	←
Styrene	31	←	←	←	←	←	←
Methylmethacrylate	21	←	←	←	←	←	←
2,2'-azobisisobutylnitrile	1	←	←	←	←	←	←
Physical properties							
Resin acid value	31	31	32	33	30	30	31
Weight average molecular weight	8500	9000	8700	9000	8800	8600	9000
Glass transition temperature (°C)	47	45	43	50	42	40	39

Production No.	8
Mixed solution added dropwise	
Acrylic resin	A#
N-butoxymethylacrylate	30
Acrylic acid	5
2-ethylhexylmethacrylate	30
N-butylacrylate	35
Benzoyl peroxide	6
Physical properties	
Resin acid value	40
Weight average molecular weight	8500
Glass transition temperature (°C)	47

[Example IV-1]

3.1 parts (amount corresponding to 1.0 mol with respect to 1 mol of carboxylic group in the acrylic resin) of N,N-dimethylaminoethanol was added to 70 parts of the acrylic polyol resin (A-1) solution having a solid content of approximately 71% obtained in the Production Example IV-1 and 13 parts of the acrylic resin (A#) solution having a solid content of approximately 77% obtained in the Production Example IV-8, followed by uniformly mixing at 50°C and, followed by adding 50 parts of Nikalac N-6215 (a methyletherized methylolmelamine-benzoguanamine cocondensed resin manufactured by Sanwa Chemical, Ltd.) as an aminoplasto resin (IV-B) and 0.7 part of Nacure (Nacure) 5225 (a curing catalyst manufactured by King Industries, Ltd., USA). After having sufficiently mixed at 30°C, deionized water was gradually added to prepare a water-based coating having a solid content of approximately 40%.

[Examples IV-2 to IV-3] and [Comparative Examples IV-1 to IV-4]

The same procedures were conducted as in the Example IV-1, except that respective acrylic polyol resin solutions, aminoplasto resin (IV-B), and formulation amount (solid content) of the resins were changed as shown in Table IV-9, and amount of N,N-dimethylaminoethanol were changed to an amount corresponding to 1.0 mol with respect to 1 mol of carboxylic group in the acrylic resin to be employed to prepare a water-based coating.

<Preparation of a test plate to be coated>

A commercially supplied ink was coated on an aluminum plate having the thickness of 0.3 mm, and respective water-based coatings obtained in the Examples and Comparative Example were coated by wet-on-wet so that thickness of a coating layer becomes 5 μ m after having dried, subsequently, baking was conducted for 90 seconds at a condition in which a maximum temperature being capable of attaining in materials becomes 200°C to obtain a coated plate. It is to be noted that it was not able to coat the coatings in the Comparative Example 2 and Comparative Example 9 because of a high viscosity.

In relation to thus-obtained coated plate, there were tested physical properties of the coating layer and a wet ink-adaptability. Test results are shown in Table IV-9.

Tests were conducted according to the methods described below.

Pencil Hardness: A pencil scratch test regulated in JIS K5400 8. 4.2 (1990) was conducted on the coated plate, and evaluated by scratches.

Retort resistance: A coated plate was immersed in a deionized water. A whitening condition of the coated layer and the pencil hardness

were checked after having treated for 30 minutes at 125°C in an autoclave.

The whitening condition of the coated layer was visually evaluated according to the following rules.

- ◎: quite no whitened
- : slightly whitened
- : very whitened
- x: whitened at all surface

After the coated plate was pulled up from water and placed in warm water of 80°C for 3 minutes, the pencil scratch test was conducted in warm water of 80°C according to JIS K-5400 8. 4. 2 (1990), and the coated layer was evaluated by scratches.

Processability: Test in relation to the coated plate was conducted at conditions of drop weight of 300 g, an edge diameter in a striking pin of 1/2 inch, and drop height of 20 cm according to a Dupon't style impact test by JIS K5400 8. 4. 2 (1990). Cracks of the coated layer were visually observed at an impact portion and a periphery thereof.

- ◎: Cracks are not observed.
- : Cracks are slightly observed.
- : Cracks are very observed at an impact portion.
- x: Cracks are very observed also at a periphery of an impact portion.

Adhesion: 100 pieces of cross-hatches of 1 mm x 1 mm were made on the coated plate according to a cross-hatched test by JIS K-5400 8. 5. 2 (1990), and a cellophane tape was stuck on the surface, and it was evaluated by counting the number of the cross-hatches remained after having abruptly stripped.

100 means that the coated layer was not stripped at all.

Wet ink adaptability: Finishing outer appearance of the coated plate was observed.

⊙: Ink does not blur, and does not become dim.

x: Ink blurs,
and becomes dim.

[Table IV-9]

Example No.	1	2	3	4	5	6	7
Acrylic poyol resin	A-1	A-2	A-3	A-1	A-2	A-3	A-4
amount	50	←	←	←	←	←	←
Acrylic resin	A#	←	←	←	←	←	←
amount	10	←	←	←	←	←	←
Amino plasto resin							
Nikalak-N-6215	40	←	←	←	←	←	←
Properties of coating layer							
Pencil hardness	4H	4H	4H	4H	3H	2H	2H
Retort property: whitening	⊙	⊙	⊙	⊙	○	○	△
Pencil hardness	2H	2H	2H	2H	H	HB	B
Processability	○	⊙	⊙	△	⊙	⊙	⊙
Adhesion	100	100	100	80	100	100	100
Wet ink adaptability	⊙	⊙	⊙	△	⊙	⊙	⊙

It is confirmed that the melamine-curable water-based coating composition is excellent in physical properties of the coating layer and wetting adaptability, which is composed of an acrylic polyol resin (A) obtained using the above-described hydroxyethyl(meth)acrylate composition (a) modified by a small amount of lactones and the aminoplasto resin (IV-B).

Example V

1. Preparation of a coating

In a coating (C series) and a comparative coating (SC series), there were employed a resin (A-1) obtained in Reference Example 5 and a resin (A-2) obtained in Reference Example 6 which are shown in Table 5, and respective resins (RA-1)-(RA-6) obtained in Comparative Reference Examples 6-11.

These acrylic polyol resins (A-1) - (RA-6) were formulated with the following substances to obtain a coating.

	<u>part</u>
Acrylic polyol resin	100
Super Bekkamine L-121-60	28
P-198	9
Butyl acetate	15
Xylene	15
Tinuvin 384	3
Tinuvin 123	1.5
<u>Modaflow</u>	<u>0.45</u>

In the above descriptions, P-198 (manufactured by Dainippon Ink, Ltd.) is a mixture of monobutyl phosphate with dibutyl phosphate.

A white enamel base was obtained by kneading for 60 minutes in a sand mill based on the above-described formulation, and an acrylic urethane coating was prepared by formulating a desired amount of a curing agent.

2. Formulation of a multi-layered type elastic acrylic emulsion coating

	<u>part</u>
Boncoat 3663	432.0
Demor EP (Kao Atlas)	6.0
Ethyleneglycol (Mitsubishi Kagaku)	4.3
Adekanate B-187 (Asahi Denka)	13.0
Celltop HP-103 (Teikoku Kako)	4.3
Calcium carbonate NS-100 (Nitto Funka)	380.5
ASP-600 (ENGEL HARD)	67.7
Taipe R-550 (Ishihara Sangyo)	13.0
5% Highmetrose	
90SH-1500 (Shin-etsu Kagaku)	28.9
Adekanol UH-420 (Asahi Denka)	2.7
<u>water</u>	<u>47.6</u>
Total	1,000.0

Evaluation of properties of a coating

1. Preparation of a test piece

As a test piece, a test piece molded from a polyolefin-based resin (X50 manufactured by Mitsui Kagaku) was washed by isopropylalcohol, and washed by a petroleum benzine.

2. Coating onto a test piece

(1) A primer (Primax No. 1500 manufactured by Nihon Yushi) was coated in 15 μ m onto the test piece and dried, and Primax No. 5500 (manufactured by Nihon Yushi) was coated as a base coating.

Subsequently, a clear coating prepared as hereinabove was diluted by a mixed thinner of xylene and Solvesso 100 as being adjusted to 16 seconds in Ford cup No. 4, followed by coating the clear coating

onto the test piece in wet-on-wet by air-spraying so that a dried coating layer becomes $30\mu\text{m}$ in the clear coating. After having placed for 10 minutes at a room temperature, it was dried by heating at 120°C for 30 minutes and 100°C for 30 minutes, and properties of the coating layer were measured after 24 hours. It is to be noted that a test in the case of coating a clear coating without using a primer is as follows. A base coat coating X was diluted by a thinner of toluene/ethyl acetate (weight ratio of 60/40) as being adjusted to 13 seconds in Ford cup No. 4, followed by air-spraying so that a dried coating layer becomes $15\mu\text{m}$.

Subsequently, respective coatings prepared as hereinabove were diluted by a mixed thinner of xylene and Solvesso 100 as being adjusted to 16 seconds in Ford cup No. 4, followed by coating the clear coating onto the test piece in wet-on-wet by air-spraying so that a dried coating layer becomes $30\mu\text{m}$ in the clear coating. After having placed for 10 minutes at a room temperature, it was dried by heating at 120°C for 30 minutes and 100°C for 30 minutes, and properties of the coating layer were measured after 24 hours.

Preparation of a base coat coating X

(a) Preparation of a grafted chlorinated polyolefin oligomer X having a primary hydroxyl group

A four-necked flask equipped with an agitating device, a thermometer, an tube for supplying an inert gas, a dropping funnel, and a reflux device was charged with 494 parts of toluene and 250 parts of Hardlene 14ML (a chlorinated polyolefin manufactured by Toyo Kasei: chlorine content of 26%), followed by temperature elevating to 100°C

while agitating. Subsequently, there was added dropwise a mixture composed of 142 parts of Placel FM-3, 104 parts of isobonylmethacrylate, 6 parts of benzoylperoxide, and 4 parts of azobisisobutyronitrile over 3 hours, and reaction was further continued for 6 hours to obtain the above-described grafted chlorinated polyolefin oligomer X.

(b) Preparation of a base coat coating X

Formulation was conducted as follows.

	<u>Part</u>
Oligomer X	249
Super Bekkamine L-121-60	50
P-198	9
Butyl acetate	15
Xylene	15
Tinuvin 384	3
Tinuvin 123	1.5
Aluminum paste	15
<u>Modaflow</u>	<u>0.45</u>

2. Evaluation method of properties

(1) Water resistance test

A molded article coated was partially immersed in warm water at 50°C for 10 days. After having taken out, there was observed the presence or absence of adhesion and a blister.

Herein, test pieces having many peeling or blisters were evaluated as x, test pieces not having peeling or having slight blisters were evaluated as , and test pieces not causing peeling and blisters were evaluated as O.

(2) Gloss retention test

There was conducted an accelerating weatherability test by Sunshine-weatherometer (manufactured by Suga Shikenki), there was measured a retention ratio (%) of a 60°-mirror surface glossiness after 1000 hours according to JIS K5400 (1979), and there was measured an adhesion test according to JIS K5400 (1976) 6.15. Test pieces having gloss retention ratio of not less than 80% and excellent adhesion were evaluated as O, test pieces having gloss retention ratio of not less than 70 and less than 80% and excellent adhesion were evaluated as , and test pieces having gloss retention ratio of less than 70% and peeling in adhesion test were evaluated as x.

(3) Gasoline resistance

A molded article coated was partially immersed in a regular gasoline (Nisseki Silver gasoline manufactured by Nihon Sekiyu) at 20°C. After having taken out, a swelling property was visually evaluated. Test pieces showing remarkable swelling were evaluated as x, test pieces showing slight swelling were evaluated as , and test pieces not showing swelling so much were evaluated as O.

(4) Acid resistance test

0.2 ml of 5%-sulfuric acid aqueous solution was dropped on a coating layer, followed by drying at 40°C for 30 minutes and visually observing a condition of the coating layer. Test pieces showing marks were evaluated as x, test pieces slightly showing marks were evaluated as , and test pieces not showing marks were evaluated as O.

(5) Solid content in a coating

In a lower solid content in a coating, it is more difficult to prepare a thick coating layer. In the clear coating and solid color

coating, a coating having not more than 30% of solid content was evaluated as x, a coating having not less than 30 and not more than 35% were evaluated as Δ , a coating having not less than 35 and not more than 40% were evaluated as O, and a coating exceeding 40% were evaluated as \odot .

(6) Pot life

It was measured according to JIS K5400 (1999) 4.9.

Physical properties of a coating layer were measured as follows.

Coating: An acrylic urethane coating obtained was diluted by a solvent of xylene/butyl acetate=60/40 to a viscosity being capable of coating, and spray-coated onto respective base materials so that layer thickness becomes 70-75 μ m after drying. Curing for drying was conducted by placing at a room temperature for 2 weeks.

(7) Extension, tensile strength test: An acrylic urethane coating as prepared hereinabove was coated on an acrylic emulsion dried coating layer having a layer thickness of approximately 1 mm prepared using an elastic acrylic emulsion coating obtained hereinabove, and it was dried at an ordinary temperature for 2 weeks to prepare a coating layer. Using the coating layer, measurement was conducted according to JIS A6910 (1984) 5. 13.

(8) Deterioration test in extension: Measurement was conducted according to JIS A6910 (1984) 5. 13 using a multi-layered coating layer prepared in the (7).

(9) Adhesion strength: Measurement was conducted according to JIS A6910 (1984) 5. 8 using a multi-layered coating layer prepared in the (7).

(10) Cold cycle test: It was conducted according to JIS A6910

(1984) 5. 9

(11) Dispersibility of pigments

(a monochromatic base)

* carbon black:

Royal Sbetramark I (Columbia Carbon, Ltd.) PWC5%

* Shinkasya Red:

Fastogen Super Red BN (Dainippon Ink Kagaku, Ltd.) PWC10%

* Dianine Blue:

Fastogen Blue FGS (Dainippon Ink Kagaku, Ltd.) PWC10%

Coagulation property and a thixotropic property were visually judged in relation to an original color enamel base kneaded under special conditions.

(Mixed color base)

The above-described respective color enamel bases were formulated so that it becomes white/original color=98/2 (pigments ratio), and a curing agent was formulated. After having diluted by a solvent, it was spray coated. After having confirmed dryness by finger touch, the same coating partially remained was flow-coated on an approximately half portion in the coated plate and cured.

Quality of dispersibility was judged by a color difference (E) between a spraying portion and flow coating portion. Smaller value is more excellent in dispersibility.

(12) Staining resistance:

(i) Staining by a felt pen:

After having been stained by a felt pen, sample was placed at room temperatures for 2 hours, and wiped by a solvent of petroleum/ethanol=1/1, and a staining level was visually judged.

Herein, ◎: Marks are not quite remained. ○: Marks are slightly remained. : Marks are fairly remained. x: Marks are very remained.

(ii) Staining by wet carbon:

Water dispersion containing 3% of carbon was made, and it was softly applied by cotton, and it was placed at an ordinary temperature for 1 day. After having washed by water, marks were visually judged.

Rules for judgement are the same as in the (i).

From the Examples and Comparative Examples, it is evident that in the case that a coating having a low proportion of the adducts in which not less than 2 mol of ϵ -caprolactone is added is employed as, for example, a top-coating material for cars, there can be obtained a coating layer which is well-balanced among excellent workability, a hardness of a coating layer, a finishing outer appearance, weatherability, acid resistance, staining resistance, gloss, flexibility, and abrasion resistance.

Example VI.

Reference Example VI-7 [Preparation Example of a copolymer (VIA-1)]

A four-necked flask replaced with nitrogen gas was charged with 294 parts of methylethylketone, followed by maintaining at 75°C while agitating. Subsequently, there was added dropwise a mixture composed of 36.9 parts of methacrylic acid, 90.0 parts of styrene, 42.6 parts of butyl acrylate, 40.5 parts of an ϵ -caprolactone-modified acrylic monomer obtained in the Example 1, 90.0 parts of lauryl methacrylate, and 6.0 parts of Perbutyl O [tert-butylperoxy-2-ethylhexanoate manufactured by Nihon Yushi, Ltd.] over 2 hours. Further, reaction was conducted at the same temperature for 5 hours to obtain a copolymer (VIA-1) having nonvolatile components of 50.0% by weight, an acid value of 80 and, further, hydroxyl value of 58 (unit: mg-KOH/g, hereinafter,

the same).

Reference Example VI-8 [Preparation Example of a copolymer (VIA-2)]

A four-necked flask replaced with nitrogen gas was charged with 870 parts of methylethylketone, followed by maintaining at 80°C while agitating. Subsequently, there was added dropwise a mixture composed of 207 parts of styrene, 150 parts of lauryl methacrylate, 72 parts of an ϵ -caprolactone-modified acrylic monomer obtained in the Example 3, 168 parts of butyl methacrylate, and 30 parts of "Perbutyl O" over 4 hours. Further, polymerization reaction was continued over 4 hours while agitating to obtain a resin having hydroxyl groups, which has a number average molecular weight of 26,000 and nonvolatile components of 40%.

Subsequently, 6.8 parts of methacrylic anhydride was added to the polymer solution, followed by agitating for 4 hours to obtain a vinyl group-modified resin (VIB-1) having hydroxyl groups. After that, the same flask as in the above-described flask was charged with 175 parts of the resin (VIB-1), followed by elevating temperature to 80°C while agitating. There was added dropwise a mixture of 9.2 parts by weight of methacrylic acid, 7.6 parts of styrene, 7.5 parts of lauryl methacrylate, 3.4 parts of butyl acrylate, 2.3 parts of 2-hydroxyethyl methacrylate, 4.5 parts of "Perbutyl O", and 20 parts by weight of methylethylketone over 4 hours to allow to continue a polymerization.

Also after that, agitation was allowed to continue over 2 hours to obtain a vinyl-based copolymer (VIA-2). Non volatile components were 45.6%.

Reference Example VI-9 [Preparation Example of a copolymer (VIA-3)]

A reaction vessel replaced with nitrogen was charged with 870

parts of methylethylketone, followed by elevating a temperature to 80°C while agitating. Into the vessel, there was added dropwise a mixture composed of 180 parts of styrene, 150 parts of lauryl methacrylate, 78 parts of butyl acrylate, 72 parts of an ϵ -caprolactone-modified acrylic monomer obtained in the Example 3, 120 parts of glycidyl methacrylate, and 30 parts of "Perbutyl O" over 4 hours to allow to continue polymerization. Further, agitation was continued over 4 hours to obtain a polymer solution of a resin having glycidyl groups and hydroxyl groups, which has a number average molecular weight of 20,000 and nonvolatile components of 40%.

Subsequently, 6.8 parts of methacrylic anhydride was added to the polymer solution, followed by agitating at 60°C for 6 hours and adding 0.5 part of water to obtain a vinyl-modified resin (VIB-2) having hydroxyl groups, in which glycidyl groups are remained.

After that, the same vessel as in the above-described vessel was charged with 300 parts of the resin (VIB-2), followed by elevating temperature to 80°C while agitating.

Subsequently, there was added dropwise a mixture composed of 39.2 parts of methacrylic acid, 27.0 parts of styrene, 45.0 parts of lauryl methacrylate, 41.0 parts of butyl acrylate, 27.8 parts of 2-hydroxyethyl methacrylate, 27.0 parts of "Perbutyl O", and 40.0 parts by weight of methylethylketone over 4 hours to allow to conduct a polymerization. Also after that, agitation was allowed to continue over 2 hours to obtain a vinyl-based copolymer (VIA-3). Non volatile components were 54.8%.

Reference Example VI-10 [Preparation Example of a copolymer (IVA-4)]

A reaction vessel replaced with nitrogen was charged with 150

parts of the resin (VIB-1) obtained in the Reference Example IV-8 and the resin (VIB-2) obtained in the Reference Example VI-10, respectively, followed by elevating temperature to 80°C while agitating.

Subsequently, there was added dropwise a mixture composed of 39.2 parts of methacrylic acid, 27.0 parts of styrene, 45.0 parts of lauryl methacrylate, 41.0 parts of butyl acrylate, 27.8 parts of 2-hydroxyethyl methacrylate, 27.0 parts of "Perbutyl O", and 40.0 parts by weight of methylethylketone over 4 hours to allow to conduct a polymerization. Also after that, agitation was allowed to continue over 2 hours to obtain a vinyl-based copolymer (VIA-4). Non volatile components were 54.8%.

Reference Example VI-11 [Preparation Example of a copolymer (VIA-5)]

A reaction vessel was charged with 62.5 parts of a polycaprolactone diol having a number average molecular weight of 1,250, 167.8 parts of "AOGX 68" [a long chain olefin glycol manufactured by Daicel Chemical Industries, Ltd., hydroxyl value=290], and 111 parts of 1-isocyanate-3-isocyanatemethyl-3,5,5-trimethylcyclohexane (IPDI), and temperature was elevated to 110°C under nitrogen atmosphere while agitating, followed by maintaining at the temperature for 60 minutes.

After that, the temperature was decreased to 80°C, and there were fed 33.5 parts of dimethylol propionic acid, 160.6 parts of ethyl acetate, and 0.05 part of tin octoate, followed by allowing to continue a reaction at 75°C for 7 hours. After the completion of the reaction, 214.2 parts of ethyl acetate was added to obtain a urethane resin solution having hydroxyl groups which has non volatile components of 50%.

2.6 parts of methacrylic anhydride was fed into the resin solution, followed by agitating at 75°C for 4 hours to obtain a vinyl-modified

resin (VIB-3) having hydroxyl groups.

Subsequently, 100 parts of the resin (VIB-3) was fed into a same reaction vessel replaced with nitrogen, followed by elevating a temperature to 75°C while agitating. There was added dropwise a mixture composed of 15.4 parts of methacrylic acid, 23.3 parts of styrene, 22.4 parts of isobutyl methacrylate, 5.5 parts of 2-hydroxyethyl methacrylate, 50.1 parts of the ϵ -caprolactone-modified acrylic monomer obtained in the Reference Example 3, 9.3 parts of "Niper BW" [benzoyl peroxide manufactured by Nihon Yushi, Ltd.], and 116.7 parts of ethyl acetate over 4 hours to allow to conduct a polymerization reaction. Also after that, agitation was allowed to continue over 4 hours to obtain a vinyl-based copolymer (VIA-5). Nonvolatile components were 48.6%.

Reference Comparative Example VI-12 [Preparation Example of a copolymer (VIRA-1)]

The same polymerization was followed as in the Reference Example VI-7 except that the ϵ -caprolactone-modified acrylic monomer obtained in the comparative Example 1 was employed in place of 40.5 parts of the ϵ -caprolactone-modified acrylic monomer obtained in the Example 1 to obtain a vinyl-based copolymer having non volatile components of 50.0%, an acid value of 80, and a hydroxyl value of 58.

Reference Comparative Example VI-13 [Preparation Example of a vinyl-based copolymer (VIRA-2)]

The same polymerization was followed as in the Reference Example VI-11 except that "Placel FM3" [a lactone-modified hydroxyethylmethacrylate manufactured by Daicel Kagaku Kogyo, Ltd.] was employed in place of the ϵ -caprolactone-modified acrylic monomer

obtained in the Comparative Example 3 to obtain a vinyl-based copolymer having non volatile components of 50.0%, an acid value of 80, and a hydroxyl value of 58.

Example VI-1

In a reaction vessel which is vigorously agitated there were mixed 200 parts of the vinyl-based copolymer (VIA-1) which is an acrylic polyol resin, 39.7 parts of "Vernok 980" [a polyisocyanate manufactured by Dainippon Ink Kagaku Kogyo, Ltd., nonvolatile components=75.6%], 100 parts of methylethylketone, and 5.0 parts of triethylamine, and 300 parts of distilled water was gradually added to the vessel. During a reaction, 0.02 part of dibutyltin dilaurate was added immediately before phase inversion, and 200 parts of distilled water was added after phase inversion.

Subsequently, solvents were distilled off at reduced pressure, and heating was continued at 60°C for 1 hour to allow to accelerate a crosslinking in inside of particles. After that, water was partially distilled off at reduced pressure to obtain a water dispersion of crosslinked particles having 31.0% of nonvolatile components.

After that, the water dispersion of crosslinked particles was partially taken out, and tetrahydrofran was added in a 100 times amount and, as a result, it was muddy without transparently dissolving.

Further, the water dispersion was maintained at 50°C for 20 days, and a change was observed with a lapse of time and, as a result, any change was not observed in stability of dispersibility.

However, when ethyleneglycol monobutylether was added in an amount corresponding to 20% based on solid components in the water dispersion, tendency of viscosity increase was observed in a system after 20 days

at 50°C.

It is to be noted that it showed an average molecular weight of 570 between crosslinking points in thus-obtained crosslinked particles, which is a designed value. Still further, a solvent was added in an amount corresponding to 20% based on solid components and, as a result, a film-forming temperature was not more than a room temperature.

Example VI-2

The same procedures were followed as in the Example IV-1, except that there were employed 219.3 parts of the vinyl-based copolymer (VIA-2) which is an acrylic polyol resin, 39.7 parts of "Vernok 980", 100 parts of methylethylketone, and 10.8 parts of triethylamine. As a result, nonvolatile components were 31.6% in thus-obtained water dispersion of crosslinked particles and a dispersion state was also excellent.

Subsequently, the water dispersion of crosslinked particles was partially taken out, and tetrahydrofran was added in a 100 times amount and, as a result, it was muddy without transparently dissolving. Further, the water dispersion was maintained at 50°C for 20 days, and a change was observed with a lapse of time and, as a result, any change was not observed in stability of dispersibility. Likewise, when ethyleneglycol monobutylether was added in an amount corresponding to 20% based on solid components in the water dispersion, tendency of viscosity increase was not observed in a system even after 20 days at 50°C. It is to be noted that it showed an average molecular weight of 630 between crosslinking points in thus-obtained crosslinked particles, which is a designed value. Still further, a solvent was added in an amount corresponding to 20% based on solid components and,

as a result, a film-formable temperature was not more than a room temperature.

Example VI-3

The same procedures were followed as in the Example IV-1, except that there were employed 182.5 parts of the vinyl-based copolymer (VIA-3) which is an acrylic polyol resin, 26.5 parts of "Vernok 980", 150 parts of methylethylketone, and 15.3 parts of triethylamine. As a result, nonvolatile components were 30.5% in thus-obtained water dispersion of crosslinked particles and a dispersion state was also excellent.

Subsequently, the water dispersion of crosslinked particles was partially taken out, and tetrahydrofran was added in a 100 times amount and, as a result, it was muddy without transparently dissolving. Further, the water dispersion was maintained at 50°C for 20 days, and a change was observed with a lapse of time and, as a result, any change was not observed in stability of dispersibility. Likewise, when ethyleneglycol monobutylether was added in an amount corresponding to 20% based on solid components in the water dispersion, tendency of viscosity increase was not observed in a system even after 20 days at 50°C. It is to be noted that it has an average molecular weight ranging in 510-680 between crosslinking points in the crosslinked particles, which is a designed value, and which only slightly changes through reaction between glycidyl groups.

Still further, a solvent was added in an amount corresponding to 20% based on solid components and, as a result, a film-forming temperature was not more than room temperatures.

Example VI-4

The same procedures were likewise followed as in the Example IV-1, except that there were employed 182.5 parts of the vinyl-based copolymer (VIA-4) which is an acrylic polyol resin, 26.5 parts of "Vernok 980", 150 parts of methylethylketone, and 15.3 parts of triethylamine and, thus-obtained water dispersion of crosslinked particles has nonvolatile components of 32.3% in thus-obtained water dispersion of crosslinked particles and a dispersion state was also excellent.

Subsequently, the water dispersion of crosslinked particles was partially taken out, and tetrahydrofran was added in a 100 times amount and, as a result, it was muddy without transparently dissolving. Further, the water dispersion was maintained at 50°C for 20 days, and a change was observed with a lapse of time and, as a result, any change was not observed in stability of dispersibility.

Likewise, when ethyleneglycol monobutylether was added in amount corresponding to 20% based on solid components, any change was not observed in viscosity properties even after 20 days at 50°C. It is to be noted that it has an average molecular weight ranging in 580-680 between crosslinking points in the crosslinked particles, which is a designed value, and which only slightly changes through reaction between glycidyl groups.

Still further, a solvent was added in an amount corresponding to 20% based on solid components and, as a result, a film-forming temperature was not more than room temperatures.

Example VI-5

The same procedures were followed as in the Example 1, except that there were employed 205.8 parts of the vinyl-based copolymer (VIA-5) which is an acrylic polyol resin, 39.7 parts of "Vernok 980",

150 parts of methylethylketone, and 10.8 parts of triethylamine and, as a result, nonvolatile components were 35.3% in thus-obtained water dispersion of crosslinked particles and a dispersion state was also excellent.

Subsequently, the water dispersion of crosslinked particles was partially taken out, and tetrahydrofran was added in a 100 times amount and, as a result, it was muddy without transparently dissolving. Further, the water dispersion was maintained at 50°C for 20 days, and a change was observed with a lapse of time and, as a result, any change was not observed in stability of dispersibility.

Likewise, when ethyleneglycol monobutylether was added in an amount corresponding to 20% based on solid components in the water dispersion, any change was not observed in viscosity properties even after 20 days at 50°C. It is to be noted that it showed an average molecular weight of 630 between crosslinking points in the crosslinked particles, which is a designed value.

Still further, a solvent was added in an amount corresponding to 20% based on solid components and, as a result, a film-forming temperature was not more than room temperatures.

Example VI-6

A 4-necked flask replaced with nitrogen was charged with 250 parts of "Unicef PT-200" [a polytetramethylene glycol having $M_n=2,000$ manufactured by Nihon Yushi, Ltd.] and 55.5 parts by weight of isophorone diisocyanate, and a reaction was conducted at 120°C for 30 minutes. 0.05 part of tin octoate was supplied, and the reaction was further conducted for 60 minutes at the same temperature. After lowering the temperature to 80°C, 182.5 parts of methylethylketone and 33.5 parts

of dimethylol propionic acid were supplied, and a reaction was conducted at 80°C for 6 hours to obtain a urethane prepolymer having nonvolatile components of 65%, an acid value of 41.4, and an isocyanate group content of 3.0%.

After that, there were sufficiently mixed 200 parts of the polymer, 51.6 parts of "Vernok 980", 100 parts of methylethylketone, and 5.0 parts of triethylamine while sufficiently agitating, and 600 parts of distilled water was added while continuing agitation and, subsequently, there was also added an aqueous solution in which 12 parts of diethylene triamine is dissolved in 100 parts of distilled water, and solvent and water were partially distilled off at 60-70°C while maintaining a system at a reduced pressure to obtain a water dispersion of crosslinked particles having nonvolatile components of 31.0%.

Subsequently, 194 parts of thus-obtained water dispersion of crosslinked particles, 407 parts of distilled water, and 12 parts of toluene were added into a 4-necked flask replaced with nitrogen, followed by elevating a temperature to 80°C. After that, there were added dropwise over 4 hours a solution in which there were mixed 4 parts of allyl methacrylate, 13 parts of methylmethacrylate, 13 parts of butylmethacrylate, and the ϵ -caprolactone-modified acrylic monomer obtained in the Example 4 and an aqueous solution in which there were mixed 0.15 part of ammonium persulphate is dissolved in 20 parts of distilled water, respectively, and a polymerization was conducted.

Also after that, agitation was continued for 2 hours at the same temperature. Subsequently, solvent and water were partially distilled

off at a reduced pressure to obtain acryl/urethane composite crosslinked particles having nonvolatile components of 32.7%.

Subsequently, water dispersion of the crosslinked particles was partially taken out, and a 100 times amount of tetrahydrofran was added and, as a result, it was whitened without transparently dissolving. Further, a change with a lapse of time was observed while maintaining the water dispersion at 50°C for 20 days and, as a result, any change was not observed in dispersion stability at all. Likewise, when ethyleneglycol monobutylether was added in amount corresponding to 20% based on solid components in the water dispersion, any change was not observed in viscosity properties even after 20 days at 50°C. It is to be noted that it showed an average molecular weight of 500 between crosslinking points in the crosslinked particles, which is a designed value.

Still further, a solvent was added in an amount corresponding to 20% based on solid components and, as a result, a film-forming temperature was not more than room temperatures.

Comparative Example VI-1

The same procedures were likewise followed as in the Example 1, except that the vinyl-based copolymer (VIRA-1) was employed in place of the vinyl-based copolymer (VIA-1).

Comparative Example VI-2

The same procedures were likewise followed as in the Example 1, except that the vinyl-based copolymer (VIRA-2) was employed in place of the vinyl-based copolymer (VIA-5) in the Example VI-5.

Comparative Example VI-3

The same procedures were likewise followed as in the Example 1,

except that the vinyl-based copolymer (VIRA-1) was employed in place of the ϵ -caprolactone-modified acrylic monomer obtained in the Example 4 in the Example VI-6.

Comparative Examples VI-4 and VI-5

As a conventional type of method for forming a coating layer, there are employed a commercially supplied baking type thermosetting coating composed of an acrylic resin/melamine resin and a commercially supplied ordinary temperature-curing type coating composed of an acrylic resin/polyisocyanate resin, respectively, and both are a resin composition for a top coating for cars.

Application Examples VI-1 and VI-6 and Comparative Application Examples VI-1 and VI-4

Subsequently, the respective crosslinked particles obtained in the Examples and Comparative Examples were employed solely or formulated with "MW12LF" [a melamine resin manufactured by Sanwa Chemical, Ltd., nonvolatile components=75.6%] which is a cross-linking agent, followed by spray coating on a metal plate, a white base, or an electro-deposited coating plate by a usual method, respectively, to allow to form a coating layer.

Subsequently, a variety of physical properties were evaluated in relation to respective coating layers.

Further, respective evaluations were conducted according to methods shown hereinafter.

[Boiling water resistance] Coated test plates were immersed in boiling water for 60 minutes, and surface coating conditions were visually observed and evaluated.

○: Abnormal portions are not observed at all.

△: Softening or whitening are slightly observed.

x: Softening or whitening are remarkably observed.

[Staining resistance] Coated test plates were marked by a red or black oil-soluble type felt pen. After having placed for 60 minutes, those were wiped by alcohols, and staining conditions were visually observed and evaluated.

○: Marks are almost not remained.

△: Marks are slightly remained.

x: Marks are almost not removed.

[Impact resistance] Using a Dupon't style impact tester, there was dropped a weight having 1 kg and radius of 1/2 inch in a striking pin, and impact resistance is shown by a maximum height (cm) at which cracks are not caused in coated surface.

[Chipping resistance] Using a sand blasting tester (a product manufactured by Suga Shikenki, Ltd.), a coated test plate was vertically set in a sample holder of the tester. 50 g of No. 7 crushed stones were sprayed by air pressure of 4 kg/cm² from the tester, and crushed stones were struck at right angles against the plate. After that, the test pieces were washed by water, and dried to evaluate and judge a condition of abrasion in the coating layer caused by chipping according to the following rules.

It is to be noted that the test pieces were placed in a thermostatic chamber cooled at -25°C for 20 minutes, and chipping test was conducted according to the above-described methods immediately after having taken out.

◎: Peeling and blisters of coating layer are not observed at

all.

○: Peeling and blisters of coating layer are slightly observed.

x: Peeling and blisters of coating layer are remarkably observed.

[Adhesion] 11 pieces of lines crossed at right angles were lengthwise and laterally made at an interval of 1 mm in a nearly center portion of the test pieces by a cutter knife until attaining to the plate itself, and 100 pieces of cross-hatches were made in 1 cm², and a cellophane tape was stuck on the surface, and it was visually evaluated by counting the number of the cross-hatches remained after having been abruptly stripped.

○: Peeling of coating layer is not observed at all.

△: Peeling of coating layer is slightly observed.

x: Peeling of coating layer is remarkably observed.

[Gloss] It was evaluated by a mirror surface reflection using 60°-mirror surface photometer.

[Solvent resistance] Xylene or acetone was absorbed in a felt, followed by rubbing 200 times while loading the weight of 1 kg using a rubbing apparatus. It is shown by gloss retention ratio in a surface of a coating layer.

[Acid resistance] 10% sulphric acid aqueous solution was spotted on a coating surface, and it was evaluated at 10 grades by visually observing blisters and damages of a coating layer after maintaining at 60°C for 30 minutes.

[Alkali resistance] A coated plate was immersed in 5% KOH aqueous solution at room temperatures for 100 hours, and it was visually

evaluated by a level of damages.

[Hardness] It was evaluated by pencil hardness.

[Weatherability] A coated plate was placed in "Sunshine weather-O-meter" manufactured by Suga Shikenki, Ltd., a weatherability accelerating test was conducted over 1,000 hours, and it is shown by gloss retention ratio.

[Pot life] It was measured according to JIS K5400 (1999)4.9.

From the Examples and Comparative Examples, it is evident that in the case of employing a coating having a low proportion of -caprolactone adducts containing 2 continuous chains as, for example, a top-coating material for cars, there can be obtained a coating layer which is well-balanced among excellent workability, a hardness of a coating layer, a finishing outer appearance, weatherability, acid resistance, stain resistance, gloss, flexibility, and abrasion resistance.

Example VII.

(Examples VII-1 and VII-2)

[Synthesis of an acrylic polyol (VII-A)]

A reaction vessel equipped with an agitator, a thermometer, a reflux condenser, tube for introducing nitrogen gas, and a dropping funnel was charged with 30 parts of isobutyl acetate and 9 parts of xylene, followed by elevating a temperature to 105°C while supplying nitrogen gas. After that, a mixture described hereinafter was dropped from the dropping funnel over 4.5 hours to conduct a radical polymerization. After the completion of dropping of the mixture, a solution composed of 5 parts of xylene and 0.5 part of

2,2'-azobisisobutyronitrile (AIBN) was dropped over 1 hour at 110°C.

After the completion of dropping, aging was conducted at 115 for 1.5 hour, followed by cooling to obtain an acrylic polyol resin solution (solid content of 60%) described below.

Acrylic polyol resin (VIIA 1): 25.1 parts of styrene, 5.3 parts of MMA, 32.3 parts of butyl acrylate, 4.9 parts of glycidyl methacrylate, 31.6 parts of the above-described FM0.50, 18 parts of xylene, 1.7 part of AIBN. In the acrylic polyol resin, a number average molecular weight was 9,700, and OHV was 74 mg-KOH/g.

Acrylic polyol resin (VIIA 2): The same polymerization was conducted as in the acrylic polyol resin (VIIA 1) except that FM0.75 was employed in place of the FM0.50. In the acrylic polyol resin, a number average molecular weight was 9,800, and OHV was 73 mg-KOH/g.

Acrylic polyol resin (VIIA 3): (composition) 28.1 parts of styrene, 5.3 parts of MMA, 32.3 parts of butyl acrylate, 2.0 parts of methacrylic acid, 31.6 parts of FM1.0 (an adduct in which caprolactone is added to hydroxyethylmethacrylate in 1.0 mol on an average manufactured by Daicel Kagaku kogyo, Ltd.), 18 parts of xylene, 1.7 part of AIBN. In a copolymer obtained, a number average molecular weight was 9,500, and OHV was 74 mg-KOH/g.

Acrylic polyol resin (VIIA 4): (composition) 25.1 parts of styrene, 5.3 parts of MMA, 32.3 parts of butyl acrylate, 4.9 parts of glycidyl methacrylate, 31.6 parts of FM1.0, 18 parts of xylene, 1.7 part of AIBN. In a copolymer obtained, a number average molecular weight was 9,700, and OHV was 74 mg-KOH/g.

Acrylic polyol resin (VIIA 5): (composition) 5.0 parts of dimethylaminomethacrylate, 28.5 parts of MMA, 32.3 parts of butyl

acrylate, 2.0 parts of methacrylic acid, 4.9 parts of glycidyl methacrylate, 31.6 parts of FM1.0, 18 parts of xylene, 1.7 part of AIBN. In a copolymer obtained, a number average molecular weight was 9,800, and OHV was 74 mg-KOH/g.

[Synthesis of a copolymer (VII-B) containing an alkoxysilyl group]

A reaction vessel equipped with an agitator, a thermometer, a reflux condenser, tube for introducing nitrogen gas, and a dropping funnel was charged with 45.7 parts of xylene, followed by elevating a temperature to 108°C while supplying nitrogen gas.

After that, a mixture described hereinafter was dropped from the dropping funnel over 5 hours to conduct a radical polymerization. After the completion of dropping of the mixture, 0.5 part of AIBN and 5 parts of xylene were dropped over 1 hour.

After the completion of dropping, aging was conducted at 115°C for 1.5 hour, followed by cooling to obtain a solution of a copolymer containing an alkoxysilyl group (solid content of 60%) described below.

Copolymer (VII B1) containing an alkoxysilyl group: (composition)
12.7 parts of styrene, 44.9 parts of MMA, 6.8 parts of stearyl methacrylate, 30 parts of γ -methacryloxypropyl trimethoxysilane, 4.9 parts of glycidyl methacrylate, 18.4 parts of xylene, 4.5 part of 2,2'-azobisisobutyronitrile (AIBN). In a copolymer obtained, a number average molecular weight was 6000.

Copolymer (VII B2) containing an alkoxysilyl group: (composition)
12.7 parts of styrene, 44.9 parts of MMA, 6.8 parts of stearyl methacrylate, 30 parts of γ -methacryloxypropyl trimethoxysilane, 4.9 parts of maleic anhydride, 18.4 parts of xylene, 4.5 part of

2,2'-azobisisobutyronitrile (AIBN). In a copolymer obtained, a number average molecular weight was 6000.

[Preparation of a coating]

A coating having composition shown in Table VII-7 was prepared using 36 parts of any one of the above-described acrylic polyol resins VIIA 1 to VII A5 and 24 parts of any one of the above-described copolymers VII B1 to VII B2 containing an alkoxysilyl group, respectively.

In Table VII-7, A-1120 and A-187 are a product manufactured by UCC, Co.; Tinuvin 900 is an ultraviolet ray absorbent manufactured by Ciba Geigy, AG., Tinuvin 144 is a photostabilizer manufactured by Ciba Geigy, AG.; PS399.7 is a polydimethyl siloxane having silanol group at terminals manufactured by Chisso, Co.; Solvesso #100 is an aromatic solvent having a high boiling point.

[Coating and Evaluation]

A coated plate for a test piece was prepared by coating an epoxy amide-based cationic electro-deposition primer and a middle coating surfacer for cars onto a mild steel plate degreased and treated by phosphatization (provided, a glass plate in an abrasion test). On the plate, there was coated a base coat (an acrylmelamine resin coating) a top coat clear coating having composition shown in Table No. 7 by wet-on-wet, followed by setting for 20 minutes and baking at 140°C for 30 minutes.

Thickness of a dried coating layer was approximately 15 μ m in base coat and approximately 30 μ m in the topcoat clear coating. Coated articles obtained were evaluated as described below, and results are

shown in the Table VI-7.

As a result, in the coatings composed of the composition of the present invention, an abrasion resistance is improved without loss of other properties.

Outer appearance: It was visually evaluated overall by gloss and a build feeling. ○ is excellent, △ is usual, and x is worse.

Adhesion: Cross-hatched (2 mm x 2 mm) test was conducted using a cellophane tape and, in evaluation, 25/25 is 10 scores, 0/25 is 0 score.

Hardness: It was measured according to JIS K5400.

Acid resistance: 5-6 droplets of 38% H_2SO_4 were spotted on test pieces, and the test pieces were placed at room temperature for 24 hours. After having wiped, marks were checked. ○: It is not abnormal, △: Marks are remained and sheariness is slightly caused, and x: sheariness is completely caused.

Staining resistance: An engine oil after approximately 5,000 km-running was coated on a test piece, and the test piece was placed in conditions of 50°C and 98%RH for 24 hours. After having taken out and wiped, and the test piece was compared to an untested piece.

○: no change △: slight color change, and x: distinct change

Abrasion resistance: Using a Hazemeter (a turbidimeter) NDH-300A manufactured by Nihon Densyoku Kogyo, there was measured a Haze value (Haze value before rubbing) in a glass-made base plate having a coating layer, and there was measured a Haze value (Haze value after rubbing) after having abraded at 5 cycles using stainless steel wool under a loading of 200 g, and difference was calculated. Measured value is an average value of 2 times.

Weatherability: Using Youbucon manufactured by Atlas Co., an ultraviolet ray was irradiated at 70°C for 8 hours, and an accelerating test was conducted at a cycle of water coagulation (darkness) at 50°C for 4 hours, in which a test is conducted for 7000 hour and 8000 hours, and retention ratio of gloss is evaluated.

Contact angle: A contact angle meter CA-P type manufactured by Kyowa Kaimen Kagaku, Ltd. was employed to measure a contact angle (degree) against water.

Rubbing property: MEK (methylethyl ketone) was absorbed in degreased cotton, and respective test pieces were rubbed 300 times at same conditions, and a condition was observed. Evaluation was conducted that ◎ is no change, and ○ is a condition having a small amount of scratches in the surface.

Transition of gel fraction: Coatings were coated on a fluorized resin film, respectively, and a film having a thickness of 30 μ m was prepared by baking at 140°C for 30 minutes. There were measured a gel fraction (an acetone-extracting method) of a film obtained and a gel fraction after having immersed in warmed water of 60°C for 1 month.

In the Table shown below, VII is omitted

	Example		Comparative Example			
	1	2	1	2	3	4
[Composition]						
Component A	A-1	A-2	A-3	A-5	A-4	A-4
Component B	B-1 ²	B-2	B-2	B-1	B-2	B-2
Diocetyl tin maleate	0.72	0.72	0.72	0.72	0.72	0.72
Reaction product of A-1120 with A-187	0.72	0.72	0.72	0.72	0.72	0.72
Tinuvin 900	0.36	0.36	0.36	0.36	0.36	0.36
Tinuvin 144	0.36	0.36	0.36	0.36	0.36	0.36
PS399.7	1.8	—	—	—	—	1.8
Solvesso #100	34.24	34.24	34.24	34.24	34.24	34.24
Methanol	1.8	1.8	1.8	1.8	1.8	1.8
Ortho methyl acetate	1.8	1.8	1.8	1.8	1.8	1.8
[Coating]						
Outer appearance	○	○	○	○	○	○
Adhesion	10	10	10	10	10	10
Hardness	2H	2H	2H	2H	2H	2H
Acid resistance	○	○	○	○	○	○
Staining resistance	○	○	○	○	○	○
Abrasion resistance before rubbing	0.16	0.16	0.37	0.31	0.34	0.39
(Haze value) after rubbing	2.76	2.81	3.75	3.28	3.45	3.95
Difference between before and after	2.60	2.65	3.38	2.97	3.11	3.56
Weatherability 700 hours	97	98	98	99	97	98
2800 hours	93	92	90	90	93	92
Contact angle against water	80	90	79	79	80	90
MEK rubbing property (300 times)	◎	◎	○	○	○	○
Gel fraction before immersion	95.2	95.0	95.3	95.8	95.2	95.0
after immersion	92.2	92.3	91.2	91.0	92.2	92.3

Example VIII.

[Example VIII-1]

A 500-ml glass-made flask equipped with an agitating device, a thermometer, and a water cooling condenser was charged with 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) obtained in the Example 1, 40.2 g (0.41 mol) of maleic anhydride, 0.39 g of N-methylimidazole, and 0.09 g of hydroquinone monomethylether.

Subsequently, the flask was heated while agitating and streaming air into a gas phase portion, and it was maintained at liquid temperature at 90°C for 8 hours and, an esterification reaction was further conducted

at 100°C for 3 hours.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappeared maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c-1) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 180 mg KOH/g that the product is a carboxylic group-contained acrylate monomer modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

[Example VIII-2]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 177 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-2) obtained in the Example 2 and 80.4 g (0.82 mol) of maleic anhydride were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappeared maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c-2) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 180 mg KOH/g that the product is a carboxylic group-contained acrylate monomer modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified

2-hydroxyethylmethacrylate composition (a-2).

[Example VIII-3]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 153 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-3) obtained in the Example 3 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappeared maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c-3) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 197 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-3).

[Example VIII-4]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 161 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-4) obtained in the Example 4 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappeared maleic anhydride and the

lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c-4) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 191 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-4).

[Comparative Example VIII-1]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 200 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a'-1) obtained in the Comparative Example 1 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c'-1) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 164 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

[Comparative Example VIII-2]

The quite same esterification reaction was conducted as in the

Example VIII-1, except that 200 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a'-2) obtained in the Comparative Example 2 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c'-2) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 164 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

[Comparative Example VIII-3]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 286 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a'-3) obtained in the Comparative Example 3 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c'-3) modified by a small amount of lactones. As

a result of the analysis, it was confirmed from an acid value of 123 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

[Comparative Example VIII-4]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 387 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a'-4) obtained in the Comparative Example 4 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappeared maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c'-4) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 98.4 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

[Comparative Example VIII-5]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 481 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a'-5) obtained in the Comparative Example 5 and maleic anhydride (0.82 mol) were employed

in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c'-5) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 82.0 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

[Example VIII-5]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 60.7 g (0.41 mol) of phthalic anhydride was employed in place of maleic anhydride in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear phthalic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c-5) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 154 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in which one molecule of phthalic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

[Example VIII-6]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 78.7 g (0.41 mol) of trimellitic anhydride was employed in place of maleic anhydride in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear trimellitic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c-6) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 275 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in which one molecule of trimellitic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

[Example VIII-7]

The quite same esterification reaction was conducted as in the Example VIII-1, except that 89.4 g (0.41 mol) of pyromellitic anhydride was employed in place of maleic anhydride in the Example VIII-1.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappeared pyromellitic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (c-7) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 129 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition modified by a small amount of lactones having carboxylic group in which one molecule of pyromellitic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition

(a-1).

Example IX.

[Synthesis of carboxylic group-contained acrylate monomer compositions (a'-1 to a'-7, a''-1 to a''-5) modified by a small amount of lactones]

Reference Example IX-5

A 500-ml glass-made flask equipped with an agitating device, a thermometer, and a water cooling condenser was charged with 88.4 g (a terminal hydroxyl group of 0.41 mol, hereinafter, the same) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) obtained in the Example 1, 40.2 g (0.41 mol) of maleic anhydride, 0.39 g of N-methylimidazole, and 0.09 g of hydroquinone monomethylether.

Subsequently, the flask was heated while agitating and streaming air into a gas phase portion, and it was maintained at liquid temperature at 90°C for 8 hours and, an esterification reaction was further conducted at 100°C for 3 hours.

Reaction product was a light yellowish liquid, and it was confirmed that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-1) modified by a small amount of lactones by a GPC analysis. As a result of the analysis, it was confirmed from an acid value of 180 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-1) modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

Reference Example IX-6

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 177 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-2) obtained in the Example 2 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-2) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 180 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-2) modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-2).

Reference Example IX-7

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 153 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-3) obtained in the Example 3 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed

by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-3) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 197 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-3) modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-3).

Reference Example IX-8

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 161 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-4) obtained in the Example 4 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-4) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 191 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-4) modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-4).

Comparative Reference Example IX-6

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 200 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1') obtained in the Comparative Example 1 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-1') modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 164 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-1') modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1').

Comparative Reference Example IX-7

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 200 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-2') obtained in the Comparative Example 2 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed

by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-2') modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 164 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-2') modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-2').

Comparative Reference Example IX-8

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 286 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-3') obtained in the Comparative Example 3 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-3') modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 123 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-3') modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-3').

Comparative Reference Example IX-9

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 387 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-4') obtained in the Comparative Example 4 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-4') modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 98.4 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-4') modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-4').

Comparative Reference Example IX-10

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 481 g (0.82 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-5') obtained in the Comparative Example 5 and maleic anhydride (0.82 mol) were employed in place of 88.4 g (0.41 mol) of the lactone-modified 2-hydroxyethylmethacrylate composition (a-1) in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed

by a GPC analysis that there disappear maleic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-5') modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 82.0 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-5') modified by a small amount of lactones in which one molecule of maleic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-5').

Reference IX-9

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 60.7 g (0.41 mol) of phthalic anhydride was employed in place of maleic anhydride in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappeared phthalic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-5) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 154 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-5) modified by a small amount of lactones in which one molecule of phthalic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

Reference IX-10

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 78.7 g (0.41 mol) of trimellitic

anhydride was employed in place of maleic anhydride in the Reference Example VIII-5.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear trimellitic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-6) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 275 mg KOH/g that the product is a carboxylic group-contained acrylate monomer composition (a'-6) modified by a small amount of lactones in which one molecule of trimellitic anhydride is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

Reference IX-11

The quite same esterification reaction was conducted as in the Reference Example IX-5, except that 89.4 g (0.41 mol) of pyromellitic anhydride was employed in place of maleic anhydride in the Reference Example IX-5.

Reaction product was a light yellowish liquid, and it was confirmed by a GPC analysis that there disappear pyromellitic anhydride and the lactone-modified 2-hydroxyethylmethacrylate which are a starting raw material and there is newly produced a carboxylic group-contained acrylate monomer (a'-7) modified by a small amount of lactones. As a result of the analysis, it was confirmed from an acid value of 129 mg KOH/g that the product is a tricarboxylic group-contained acrylate composition (a'-7) modified by a small amount of lactones in which one molecule of pyromellitic acid is added to the lactone-modified 2-hydroxyethylmethacrylate composition (a-1).

[Synthesis of an acrylic polycarboxylic acid resin (A'-1 to A'-6, A'-1' to A'-8)]

Synthesis Example IX-1

(Synthesis of a half-esterified acrylic polycarboxylic acid resin (A'-1))

A 3-liter reaction vessel equipped with a thermometer, an agitator, a reflux condenser, a tube for introducing nitrogen, and a dropping funnel was charged with 200 parts of xylene, 100 parts of Solvesso 100, and 100 parts of propyleneglycol monomethylether acetate followed by elevating a temperature to 125°C. Into the vessel, there were added dropwise a monomer solution composed of 100 parts of the carboxylic group-contained acrylate composition (a'-1) modified by a small amount of lactones obtained in the Reference Example IX-5, 200 parts of styrene, 580 parts of cyclohexyl acrylate, 220 parts of maleic anhydride, and 400 parts of propyleneglycol monomethylether acetate and an initiator solution composed of 100 parts of t-butylperoxy-2-ethylhexanoate and 100 parts of xylene from the dropping funnel over 3 hours. After the completion of dropwise addition, the vessel was maintained at 130°C over 30 minutes, followed by adding dropwise an initiator solution composed of 10 parts of t-butylperoxy-2-ethylhexanoate and 50 parts of xylene over 30 minutes. After the completion of dropwise addition, reaction was further continued at 130°C over 1 hour to obtain a resin varnish (nonvolatile components of 50%) containing an acrylic polyacid anhydride having a number average molecular weight of 3,800.

86 parts of methanol was added to 2060 parts of the varnish, followed by allowing to react at 70°C for 23 hours to obtain a half-esterified

varnish having an acid value of 126 mg-KOH/g-solid.

It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin obtained and there disappears an absorption (1785 cm^{-1}) by an acid anhydride.

Synthesis Example IX-2

(Synthesis of an acrylic polycarboxylic acid resin (A'-2))

The same vessel as in the Synthesis Example IX-1 was charged with 700 parts of xylene and 500 parts of Solvesso 100, followed by elevating a temperature to 130°C . Into the vessel, there were added dropwise a monomer solution composed of 380 parts of the acrylate composition (a'-1) modified by a small amount of lactones having carboxylic group obtained in the Reference Example IX-5, 300 parts of styrene, 350 parts of 2-ethylhexyl acrylate, 150 parts of isobutylmethacrylate, and 200 parts of acrylic acid and an initiator solution composed of 150 parts of t-butylperoxy-2-ethylhexanoate and 300 parts of xylene from the dropping funnel over 3 hours. After the completion of dropwise addition, the vessel was maintained at 130°C over 30 minutes, followed by adding dropwise an initiator solution composed of 20 parts of t-butylperoxy-2-ethylhexanoate and 20 parts of xylene over 30 minutes. After the completion of dropwise addition, reaction was further continued at 130°C over 1 hour, followed by removing 1100 parts of solvents to obtain a resin varnish (nonvolatile components of 70%) having a number average molecular weight of 1,800 and an acid value of 156 mgKOH/g solid.

Synthesis Example IX-3

The same vessel as in the Synthesis Example IX-1 was charged with 700 parts of xylene and 350 parts of Solvesso 100, followed by elevating

a temperature to 130°C. Into the vessel, there were added dropwise a monomer solution composed of 240 parts of the carboxylic group-contained acrylate composition (a'-1) modified by a small amount of lactones obtained in the Reference Example 5, 300 parts of styrene, 258 parts of 2-ethylhexyl acrylate, 151 parts of isobutylmethacrylate, 51 parts of acrylic acid, 240 parts of maleic anhydride, and 300 parts of propyleneglycol monomethylether acetate and an initiator solution composed of 150 parts of t-butylperoxy-2-ethylhexanoate and 150 parts of xylene from the dropping funnel over 3 hours. After the completion of dropwise addition, the vessel was maintained at 125°C over 30 minutes, followed by adding dropwise an initiator solution composed of 20 parts of t-butylperoxy-2-ethylhexanoate and 20 parts of xylene over 30 minutes. After the completion of dropwise addition, reaction was further continued at 125°C over 1 hour, followed by removing 1000 parts of solvents to obtain a varnish containing a resin (nonvolatile components of 65%) having a number average molecular weight of 2,000.

125 parts of methanol was added to 1590 parts of the varnish, followed by allowing to react at 70°C for 23 hours to obtain a varnish containing a half-esterified acrylic polycarboxylic acid resin (A'-3) having an acid value of 126 mg KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin obtained and an absorption by an acid anhydride disappears.

Synthesis Example IX-4

The quite same procedures were followed as in the Synthesis Example IX-1, except that the acrylate composition (a'-1) modified by a small amount of lactones having carboxylic group in the Synthesis Example IX-1 was replaced with 100 parts of the acrylate composition (a'-2)

modified by a small amount of lactones having carboxylic group obtained in the Reference Example IX-6 to obtain a varnish containing a half-esterified resin (A'-4) having a number average molecular weight of 1,800 and an acid value of 158 mg-KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin obtained and there disappears an absorption by an acid anhydride.

Synthesis Example IX-5

(Synthesis of an acrylic polycarboxylic acid (A'-5))

The quite same procedures were followed as in the Synthesis Example IX-2, except that the acrylate composition (a'-1) modified by a small amount of lactones having carboxylic group in the Synthesis Example IX-2 was replaced with 345 parts of the acrylate composition (a'-7) modified by a small amount of lactones having carboxylic group obtained in the Reference Example IX-7 to obtain a varnish containing a resin having a number average molecular weight of 3,800 and an acid value of 126 mg-KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin obtained and there disappears an absorption by an acid anhydride.

Synthesis Example IX-6

The quite same procedures were followed as in the Synthesis Example IX-3, except that the acrylate composition (a'-1) modified by a small amount of lactones having carboxylic group in the Synthesis Example IX-3 was replaced with 225 parts of the acrylate composition (a'-8) modified by a small amount of lactones having carboxylic group obtained in the Reference Example IX-8 to obtain a varnish containing a resin (A'-6) having a number average molecular weight of 2,000 and an acid

value of 126 mg-KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin obtained and there disappears an absorption (1785 cm^{-1}) by an acid anhydride.

Comparative Synthesis Example IX-1

(Synthesis of an acrylic polycarboxylic acid (A'-1'))

The quite same procedures were followed as in the Synthesis Example IX-2, except that the acrylate composition modified by small amount of lactones having carboxylic group in the Synthesis Example IX-2 was replaced with 414 parts of the acrylate monomer (a'-1') modified by a small amount of lactones having carboxylic group obtained in the Comparative Reference Example IX-1 to obtain a varnish containing a resin having a number average molecular weight of 3,800 and an acid value of 126 mg-KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin obtained and there disappears an absorption (1785 cm^{-1}) by an acid anhydride.

Comparative Synthesis Example IX-2

(Synthesis of an acrylic polycarboxylic acid (A'-2'))

The quite same procedures were followed as in the Synthesis Example IX-2, except that the acrylate composition modified by a small amount of lactones having carboxylic group in the Synthesis Example IX-2 was replaced with 414 parts of the acrylate composition (a'-2') modified by a small amount of lactones having carboxylic group obtained in the Comparative Reference Example IX-2 to obtain a varnish containing a resin having a number average molecular weight of 3,800 and an acid value of 126 mg-KOH/g-solid.

It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin obtained and there disappears an

absorption (1785 cm^{-1}) by an acid anhydride.

Comparative Synthesis Example IX-3

(Synthesis of an acrylic polycarboxylic acid (A'-3'))

The quite same procedures were followed as in the Synthesis Example 2, except that the carboxylic group-contained acrylate composition modified by a small amount of lactones in the Synthesis Example IX-2 was replaced with 550 parts of the carboxylic group-contained acrylate composition (a'-3') modified by a small amount of lactones obtained in the Reference Comparative Example IX-3 to obtain a varnish containing an acrylic polycarboxylic acid resin (A'-3') having a number average molecular weight of 3,800 and an acid value of 126 mg-KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin obtained and there disappears an absorption (1785 cm^{-1}) by an acid anhydride.

Comparative Synthesis Example IX-4

(Synthesis of an acrylic polycarboxylic acid (A'-4'))

The quite same procedures were followed as in the Synthesis Example IX-2, except that the carboxylic group-contained acrylate composition modified by a small amount of lactones in the Synthesis Example IX-2 was replaced with 690 parts of the carboxylic group-contained acrylate composition (a'-4') modified by small amount of lactones obtained in the Reference Comparative Example IX-4 to obtain a varnish containing an acrylic polycarboxylic acid resin (A'-4') having a number average molecular weight of 3,800 and an acid value of 126 mg-KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin and there disappears an absorption (1785 cm^{-1}) by an acid anhydride.

Comparative Synthesis Example IX-5

(Synthesis of an acrylic polycarboxylic acid (A'-5'))

The quite same procedures as in the Synthesis Example IX-2 were followed except that the carboxylic group-contained acrylate composition modified by a small amount of lactones in the Synthesis Example IX-2 was replaced with 828 parts of the carboxylic group-contained acrylate composition (a'-5') modified by a small amount of lactones obtained in the Reference Comparative Example IX-5 to obtain a varnish containing an acrylic polycarboxylic acid resin (A'-5') having a number average molecular weight of 3,800 and an acid value of 126 mg KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin and there disappears an absorption (1785 cm^{-1}) by an acid anhydride.

Comparative Synthesis Example IX-6

(Synthesis of a half-esterified acrylic polycarboxylic acid (A'-6'))

The quite same procedures were followed as in the Synthesis Example IX-1, except that the carboxylic group-contained acrylate composition (a'-1) modified by a small amount of lactones in the Synthesis Example IX-1 was not added to obtain a varnish containing a half-esterified acrylic polycarboxylic acid resin (A'-6') having a number average molecular weight of 1,800 and an acid value of 158 mg-KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin and there disappears an absorption (1785 cm^{-1}) by an acid anhydride.

Comparative Synthesis Example IX-7

(Synthesis of an acrylic polycarboxylic acid (A'-7'))

The quite same procedures were followed as in the Synthesis Example IX-2, except that the carboxylic group-contained acrylate composition (a'-1) modified by a small amount of lactones in the Synthesis Example IX-2 was not added to obtain a varnish containing an acrylic polycarboxylic acid resin (A'-7') having a number average molecular weight of 3,800 and an acid value of 126 mg KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin and there disappears an absorption (1785 cm^{-1}) by an acid anhydride.

Comparative Synthesis Example IX-8

(Synthesis of a half-esterified acrylic polycarboxylic acid (A'-8'))

The quite same procedures were followed as in the Synthesis Example IX-3 except that the carboxylic group-contained acrylate composition modified by a small amount of lactones in the Synthesis Example IX-3 was not added to obtain a varnish containing a half-esterified acrylic polycarboxylic acid resin (A'-8') having a number average molecular weight of 2,000 and an acid value of 125 mg-KOH/g-solid. It is to be noted that it was confirmed that infrared absorption spectra were measured in the resin and there disappears an absorption (1785 cm^{-1}) by an acid anhydride.

[Synthesis of a blocked carboxylic group-contained acrylic polycarboxylic acid (bA'-1 to bA'-2)]

Synthesis Example IX-7

A four-necked flask equipped with an agitating device, a thermometer, a tube for introducing an inert gas, a dropping funnel, and a cooling device was charged with 412 g (2 mol) of the acrylic

polycarboxylic acid resin (A'-1) obtained in the Synthesis Example 1, followed by adding 1000 g of tetrahydrofran, 1 mol of ethylvinyl ether (a blocking agent), and 0.2 part of 35% sulphuric acid at 35°C and allowing to react for 24 hours at the temperature.

After the completion of reaction, a product was moved to a separating funnel, followed by alkali-washing using 100 g of 10% sodium bicarbonate and 100 g of a saturated aqueous salt. After having placed, a water layer was separated and removed. This operations were repeated 20 times, and washing by a saturated aqueous salt was conducted three times by adding sodium sulphate to an organic layer at room temperatures, and tertahydrofran was removed at a reduced pressure to obtain an acrylic polycarboxylic acid (bA'-1) in which carboxylic groups are blocked by ethylvinyl ether.

Synthesis Example IX-8

The same flask as in the Synthesis Example IX-7 was charged with 2 mol of the acrylic polycarboxylic acid resin (A'-2) obtained in the Synthesis Example 2, followed by cooling at not more than 10°C by ice water and adding 300 g of tetrahydrofran and 111 g of triethylamine. A solution containing 1 mol of trimethylsilyl chloride (a blocking agent) dissolved in 100 g of tetrahydrofran was added dropwise into the flask over 30 minutes and, an ice water bath was removed at a period of 1 hour after the completion of dropwise addition, and a reaction was further continued for 10 hours. Subsequently, washing was conducted three times with 100 parts of ice water, and tetrahydrofran was removed at reduced pressures to obtain an acrylic polycarboxylic acid (bA'-2) in which carboxylic groups are blocked by trimethylsilyl chloride.

Synthesis Example IX-9

A 2-liter reaction vessel equipped with a thermometer, an agitator, a cooling device, a tube for introducing nitrogen, and a dropping funnel was charged with 300 parts of xylene and 50 parts of propyleneglycol monomethyletheracetate, followed by elevating a temperature to 125°C.

Into the reaction vessel, there were added dropwise over 3 hours a monomer solution composed of 320 parts of glycidyl methacrylate, 167 parts of styrene, 100 parts of 2-ethylhexyl acrylate, and 413 parts of FM0.75 obtained in the Reference Example IX-2 and an initiator solution composed of 120 parts of t-butylperoxy 2-ethylhexanoate and 150 parts of xylene.

After the completion of dropwise addition, the reaction vessel was maintained at 125°C over 30 minutes, followed by adding dropwise an initiator solution composed of 10 parts of t-butylperoxy 2-ethylhexanoate and 200 parts of xylene over 30 minutes.

After the completion of dropwise addition, a reaction was further continued at 125°C for 1 hour to obtain a varnish (nonvolatile components of 60%) containing a polyepoxide (IXB-1) having a number average molecular weight of 3500, an epoxy equivalent of 450, and a hydroxyl value of 95 mgKOH/g solid.

Example IX-1

(Preparation of crosslinked resin particles)

A reaction vessel equipped with an agitating and heating device, a thermometer, a tube for introducing nitrogen, a reflux condenser, and a decanter was charged with 213 parts of bishydroxyethyl taurine, 208 parts of neopentylglycol, 296 parts of phthalic anhydride, 376 parts of azelaic acid, and 30 parts of xylene, followed by elevating

a temperature. Water produced in a reaction was removed by azeotropic distillation together with xylene. Temperature in reaction was elevated to 210°C over approximately 3 hours from initiation of reflux, and the reaction was continued while agitating and dehydrating until an acid value based on a carboxylic acid attains to 135 mgKOH/g solid. After having cooled the liquid temperature to 140°C, there was added dropwise 500 parts of "Kardula E10" (glycidyl versate manufactured by Shell, Co.) over 30 minutes, followed by continuing agitation for 2 hours to complete the reaction. There was obtained a polyester resin having amphoteric ion groups which has an acid value of 55 mgKOH/g solid, a hydroxyl value of 91 mgKOH/g solid, and a number average molecular weight of 1250 in solid components.

There was prepared a monomer suspension by vigorously agitating 10 parts of the polyester resin having amphoteric ion groups, 140 parts of deionized water, 1 part of dimethylethanol amine, 50 parts of styrene, and 50 parts of ethyleneglycol dimethacrylate in a stainless steel-made beaker. Further, there was prepared an initiator aqueous solution by mixing 0.5 part of azobiscyano valeric acid, 40 parts of deionized water, and 0.32 part of dimethylethanol amine.

A reaction vessel equipped with an agitating and heating device, a thermometer, a tube for introducing nitrogen, and a reflux condenser was charged with 5 parts of the polyester resin having amphoteric ion groups, 280 parts of deionized water, and 0.5 part of dimethylethanol amine, followed by elevating a temperature 80°C. Into the reaction vessel, 251 parts of the monomer suspension and 40.82 parts of the initiator aqueous solution were simultaneously added dropwise over 60 minutes, and a reaction was further continued for 60 minutes, followed by

terminating the reaction. There was obtained an emulsion of crosslinked resin particles having particle diameter of 55 nm which was measured by a dynamic light scattering method.

Into the emulsion, xylene was added, and water was removed by azeotropic distillation at a reduced pressure. There was obtained a xylene solution of crosslinked resin particles having solid content of 20% by weight by replacing a medium with xylene.

(Preparation of a clear coating composition)

There were formulated the acrylic polycarboxylic acid resin (A'-1) obtained in the Synthesis Example X-1, a polyepoxide (IXB-1) obtained in the Synthesis Example X-9, "Sumilizer BHT" (IXC-1) and "Sumilizer TPP-R" (IXC-2) which are manufactured by Sumitomo Kagaku, Co., and there were further added 0.5 part of tetrabutyl ammonium bromide which is a curing catalyst (IXF-1), 1 part of dibutyltin bis(butylmaleate) which is a curing catalyst (IXG-1), 2 parts of "Tinuvin 900" which is an ultraviolet ray absorbent manufactured by Ciba Geigy, AG., 1 part of "Sanol LS-440" which is a photostabilizer manufactured by Sankyo, Co., and 0.1 part of "Modaflow" which is a surface controller manufactured by Monsanto Co. while agitating in Disper to prepare a curable resin composition. In the resin composition obtained, there was further added 10 parts of a xylene solution of the crosslinked resin particles prepared as described hereinabove, and viscosity was adjusted to 30 seconds by Ford Cup No. 4 using a solvent composed of butyl acetate/xylene=1/1 to obtain a clear coating composition.

Nonvolatile components and color difference were measured in order to evaluate solid content and yellowing resistance in the clear coating composition obtained.

<Nonvolatile components in a coating (NV)>

Viscosity of a coating was adjusted to 30 seconds at 20°C by Ford Cup No. 4 using a solvent, and 0.5 g of a coating composition was precisely weighed and, it was diluted by 3 cc of toluene, and then, baked at 110°C for 1 hour to measure nonvolatile components (% by weight) in the coating.

<Color difference>

A clear coating alone was coated on two pieces of a white plate so that layer thickness after drying becomes 50 μ m, and one piece was baked at 160°C for 30 minutes, and another one was baked at 140°C for 30 minutes. Using an SM color computer SM-4 manufactured by Suga Shikenki Co., "b" value was measured in a clear layer thickness of 50 μ m, and difference from the white plate, that is, b of 160°C and b of 140°C were measured, and the difference, $(\Delta b) = (\Delta b_{160^\circ\text{C}} - \Delta b_{140^\circ\text{C}})$ is defined as the color difference.

On the other hand, a cationic electro-deposition coating (Power Top U-50 manufactured by Nihon Paint, Ltd.) and a middle-coating (Orga P-2 manufactured by Nihon Paint, Ltd.) were coated on a steel plate treated by a phosphate having thickness of 0.8 mm, so that the thickness after drying becomes 25 μ m and 40 μ m, respectively, to obtain a coated test plate. And, a solvent-type high solid base coating (manufactured by Nihon Paint, Ltd.) was coated by air spraying on a coated test plate so that thickness becomes approximately 16 μ m by setting for approximately 7 minutes to form a base coat layer.

On the plate, the clear coating composition obtained was coated by an electrostatic coating machine ("Auto-Rea" manufactured by

Lansberg Gema, Co.) at an atomizing pressure of 5 kg/cm² and set for approximately 7 minutes and baked at 140°C for 25 minutes, so that the thickness after drying becomes approximately 40 μm.

It is to be noted that in the solvent-type high solid base coating, there are formulated 20 parts of an acrylic resin (nonvolatile components of 80%, a hydroxyl group value of 100 mgKOH/g solid, an acid value of 30 mgKOH/g solid, and a number average molecular weight of 1800) manufactured by Nihon Paint, Ltd., 30 parts of a polyester (nonvolatile components of 80%, a hydroxyl group value of 100 mgKOH/g solid, an acid value of 12 mgKOH/g solid, and a number average molecular weight of 2600) manufactured by Nihon Paint, Ltd., 40 parts of a melamine resin "Cymel 202" (nonvolatile components of 80%) manufactured by Mitsui Cyanamid, Co., 10 parts of a melamine resin "Cymel 327" (nonvolatile components of 90%) manufactured by Mitsui Cyanamid, Co., 10 parts of "Alupaste A160-600" (nonvolatile components of 65%) manufactured by Toyo Aluminum, Co., and 7 parts of isopropylalcohol.

<Pencil Hardness>

It was conducted according to JIS K5400 8, 4.2.

<Water resistance>

Cured coating layer obtained was immersed in a tap water at 40°C for 10 days, and coating surface was visually observed according to rules described below.

In the case that a change is not observed, it is O, in the case that marks are slightly observed, it is Δ, and in the case that a coating layer is abnormal, it is x.

<Abrasion resistance>

A flannel-made cloth having 2 cm x 2 cm was fitted at an abrasion

head of a Gakushin type dye abrasion resistance tester (manufactured by Daiei Kagaku Seiki, Co.). On the cloth, there was coated 1 g of a water dispersion containing 50% of a cleanser ("New Homing Cleanser" manufactured by Kao, Co. (abrasive particles of 87%, a surface active agent of 5%, and other components)). 500 g of weight was loaded to the abrasion head, and it was allowed to go and return 20 times over a cured coating layer, followed by measuring 20 -gloss in a test portion to calculate a gloss retention ratio (%).

<Acid resistance>

Cured coating layer obtained was immersed in 0.5 ml of 1 wt% sulphuric acid at 75°C for 30 minutes, and coating surface was visually observed according to rules described below.

In the case that an abnormality is not observed, it is 5, in the case that marks are indistinctly observed, it is 4, in the case that marks are clearly observed, it is 3, in the case that several pieces of groups of microscopic holes are observed, it is 2, and in the case that the groups of microscopic holes are observed as a whole, it is 1.

<Weatherability>

100 mW/cm² of an ultraviolet ray was irradiated in "Aisuper UV tester SUV-W13" manufactured by Iwasaki Denki, Co. for 24 hours under conditions of a black panel temperature of 63°C and humidity of 70%, and 5 cycles were repeated as 24 hours/1 cycle which is a placing time under conditions of a black panel temperature of 50°C and humidity of 100%, and after that, a coating surface was visually observed according to rules described below.

In the case that an abnormality is not observed, it is O, in the

case that cracks are slightly observed, it is Δ , and in the case that cracks are remarkably observed, it is x.

<Adhesion (a non sand-recoatibility)>

High solid base coating (manufactured by Nihon Paint, Co.) was air-sprayed on a coated plate on which an intermediate coating is coated, so that thickness of a coating layer after drying becomes approximately 16 μ m, followed by setting for approximately 7 minutes, provided that in the case of employing a water-based coating (manufactured by Nihon Paint, Co.), setting was conducted for approximately 1 minute after air-spraying, followed by preheating at 80°C for 5 minutes.

Subsequently, respective resin components were formulated in formulation (solid components) shown in Tables IX-6 and IX-7, and viscosity was adjusted to 30 seconds by Ford Cup No. 4, and a clear coating composition obtained was coated at an atomizing pressure of 5 kg/cm² using an electrostatic coating machine "Auto-Rea" (manufactured by Lansburg Gema, Co.), so that thickness of a coating layer after drying becomes approximately 40 μ m, followed by setting for approximately 7 minutes and baking at 160°C for 30 minutes.

A coated plate obtained was placed in a desiccator for 30 minutes and, after that, the above-described high solid base coating (manufactured by Nihon Paint, Co.) was likewise coated and set again on the coated plate. The above-described clear coating composition was likewise coated and set as described hereinabove on a coating layer obtained, followed by baking at 120°C for 30 minutes.

On surface of a coating layer formed, cross-cuts attaining to the coated plate passing through the coating layer were lengthwise and laterally formed using a cutter knife (NT cutter S type or A type)

at interval of 2 mm, and which has lengthwise 11 lines and laterally 11 lines, whereby, 100 pieces of squares were formed on the coating layer. A cellophane sticking (manufactured by Nichiban, Co.) tape having width of 24 mm was stuck and uniformly pressed down on the coating layer having cross-cuts while preventing formation of air bubbles by fingers. Immediately after that, one side of the sticking tape was abruptly pulled up vertically to strip the sticking tape from surface of the coating layer.

Adhesion of the coating layer was evaluated according to rules described below based on an area ratio in the coating layer stripped together with the sticking tape.

<Evaluation by area ratio stripped>

It is 5 in 0%, it is 4 in the case that it is less than 5% and complete strip of the squares is absent, it is 3 in the case that it is less than 15% and complete strip of the square is absent, it is 2 in less than 35%, and it is 1 in not less than 35%.

As a result, it was confirmed that it is able to obtain a coating layer which is excellent in abrasion resistance and the coating layer can be cured at a low temperature and, in which other properties are maintained.

Example X.

Example X-1

A four-necked flask equipped with a tube for introducing air, a thermometer, a reflux condenser, and an agitating device was charged with 1616 parts (18.8 mol) of methacrylic acid, 1610 parts (14.1 mol) of ϵ -caprolactone (ϵ -CL), 1.99 part of hydroquinone monomethylether

(HQME) which is a polymerization inhibitor, and 0.199 part of stannous chloride (SnCl_2) which is a reaction catalyst, followed by allowing to react at 100°C for 23 hours while streaming air. Reaction ratio of ϵ -caprolactone was 99.3%, and color hue of a reaction product was 20 (APHA).

Other monomers were copolymerized with a lactone-modified methacrylate composition obtained to prepare an excellent acrylic polyol resin.

Example X-2

The same procedures were likewise followed as in the Example X-1, except that 0.795 part of monobutyltin tris-2-ethylhexanate was employed as a reaction catalyst. Reaction ratio of ϵ -caprolactone was 99.5%, and color hue of a reaction product was 20 (APHA).

Other monomers were copolymerized with a lactone-modified methacrylate composition obtained to prepare an excellent acrylic polyol resin.

Comparative Example X-1

The same procedures were likewise followed as in the Example 1, except that 0.147 part of tetrabutyl titanate (TBT) was employed as a reaction catalyst, followed by allowing to react at 100°C for 64 hours while streaming air. Reaction ratio of ϵ -caprolactone was 99.6%, and color hue of a reaction product was 50 (APHA).

Comparative Example X-2

A four-necked flask equipped with a tube for introducing air, a thermometer, a reflux condenser, and an agitating device was charged with 1616 parts (18.8 mol) of methacrylic acid, 4286 parts (37.6 mol) of ϵ -caprolactone (ϵ -CL), 1.99 part of hydroquinone monomethylether

(HQME) which is a polymerization inhibitor, and 0.4 part of 1 H₂O salt of p-toluene sulphonic acid which is a reaction catalyst, followed by allowing to react at 100°C for 16 hours while streaming air. Reaction ratio of ϵ -caprolactone was 99.4%, and color hue of a reaction product was 40 (APHA).

Example X-3

A four-necked flask equipped with a thermometer, a reflux condenser, a tube for introducing nitrogen gas, and an agitating device was charged with 50 parts of butylacetate, 50 parts of toluene, and 1.0 part of ditertiary butylperoxide (DTBPO), followed by elevating a temperature to 115°C. At a period having attained to 115°C, there were added dropwise over 3 hours 17.3 parts of styrene, 17.3 parts of butyl methacrylate, 17.3 parts of butyl acrylate, 2.0 parts of methacrylic acid, 46 parts of the caprolactone-modified methacrylate composition synthesized in the Example 1, 0 part of methacrylic acid, and 1.0 part of azobisisobutyronitrile, and a reaction was further continued for 4 hours to obtain an excellent transparent acrylic polyol resin solution.

Example X-4 and Comparative Examples X-3 and X-4

The caprolactone-modified methacrylate compositions obtained in the Example X-2 and Comparative Examples X-1 and X-2 and 2-hydroxyethylmethacrylate (HEMA) were polymerized, respectively, in the same apparatus and formulation conditions as in the Example X-3. As a result, although it was able to obtain an excellent transparent acrylic polyol resin solution from the monomer obtained in the Example X-2, in the case of the monomer obtained in the Comparative Example X-1, discoloration of a reaction liquid was remarkable during the

polymerization.

In the case of preparing a material for a coating employing the monomer obtained in the Comparative Example 2, abrasion resistance is worse in a coating layer.

It is confirmed that in the above Examples 3-4 and Comparative Example 4 in which a hydroxyl value (OHV) is adjusted to 120 and T_g is adjusted to 0-10°C in the polymerization of the acrylic polyol resin, and that in Examples 3-4, a proportion of an adduct ($n=1$) in which one mol of ξ -caprolactone is added is high, and a proportion of an adduct in which two or more continuous chains of ξ -caprolactone are added is low which lowers hardness in a cured acrylic resin.

In the case of employing the adducts in which proportion of two or more continuous chains of ξ -caprolactone are added is small as, for example, a coating material for a cars top coating, there can be obtained a coating layer well-balanced among hardness of a coating layer, a finishing appearance, weatherability, acid resistance, staining resistance, gloss, flexibility, and abrasion resistance.

Example X-5

A glass-made flask equipped with an agitator, a reflux condenser, a dropping funnel, and a thermometer was charged with 144 parts (2 mol) of acrylic acid, 8 parts of 1 H₂O salt of p-toluene sulphonic acid, and 0.08 part of hydroquinone monomethylether which is a polymerization inhibitor, and 171 parts (1.5 mol) of ξ -caprolactone was dropped over 4 hours from the dropping funnel while maintaining a liquid temperature at 80°C, followed by allowing to react.

After the completion of dropwise addition, a reaction was further continued for 2 hours at the same temperature to terminate the reaction. As a result of a gaschromatographic analysis of the reaction liquid, conversion of ϵ -caprolactone was 99.3%.

In order to confirm a structure of a caprolactone-modified acrylate composition obtained, p-toluene sulphonic acid in a reaction liquid was neutralized by a methanol solution containing 1.1 times equivalent of 5%-sodium hydroxide, and an excessive amount of acrylic acid was removed at 110°C and a reduced pressure using a rotary evaporator.

The caprolactone-modified acrylate composition was obtained by filtering a reaction liquid obtained.

Physical properties of the caprolactone-modified acrylate composition (FA075A) obtained were measured. Analytical results obtained are shown as follows.

Acid value: 3.59 mg-KOH/g

Double bond: 3.68 mg equivalent/g

Number average molecular weight converted to a polystyrene by GPC: 273

Elementary analysis: C 59.9%, H 7.6%

Further, a rational formula is as follows in the caprolactone-modified acrylate composition obtained, and n is 1.76.



Example X-6

The same procedures were followed as in the Example X-5, except that 8 parts of 98% sulphuric acid was employed as an acidic catalyst to prepare a caprolactone-modified acrylate composition.

As a result of a gaschromatgraphic analysis of a reaction liquid, conversion of ϵ -caprolactone was 99.1%.

Further, the same operations were followed as in the Example X-5, and a caprolactone-modified acrylate composition was obtained by removing acrylic acid and filtering after neutralization of sulphuric acid.

The caprolactone-modified acrylate composition (FA075A2) obtained was analyzed. Results obtained are shown as follows.

Acid value: 3.61 mg-KOH/g

Double bond: 3.73 mg equivalent/g

Number average molecular weight converted to a polystyrene by GPC: 275

Example 7

The same procedures were followed as in the Example 5, except that 172 parts (2.0 mol) of methacrylic acid was employed as a radically polymerizable unsaturated monomer having carboxylic group to prepare a caprolactone-modified acrylate composition.

As a result of a gaschromatgraphic analysis of the reaction liquid obtained, conversion of ϵ -caprolactone was 99.2%.

Further, the same purification were conducted as in the Example X-5, and a caprolactone-modified acrylate composition (FM075A) was obtained.

The same analysis was conducted as in the Example X-5 in relation to the caprolactone-modified acrylate composition obtained. Results are as follows.

Acid value: 3.41 mg-KOH/g

Double bond: 3.51 mg equivalent/g

Number average molecular weight converted to a polystyrene by GPC: 287

Comparative Example X-5

The same procedures were followed as in the Example X-5, except that 236 parts (2 mol) of ϵ -caprolactone was employed to prepare a caprolactone-modified acrylate composition.

The caprolactone-modified acrylate composition (FA200A) was obtained by filtration of a reaction liquid obtained.

Physical properties were measured in relation to the caprolactone-modified acrylate composition obtained. Analytical results obtained are as follows.

Acid value: 3.30 mg-KOH/g

Double bond: 3.38 mg equivalent/g

Number average molecular weight converted to a polystyrene: 297

Elementary analysis: C 59.9%, H 7.6%

Further, "n" is 1.97 in the caprolactone-modified acrylate composition obtained.

Likewise, acrylic acid was allowed to react with ϵ -caprolactone in molar ratio of 1/0.5 to obtain FA050A for Example.

Likewise, methacrylic acid was allowed to react with ϵ -caprolactone in molar ratio of 1/0.5 to obtain FM050A for Example, and methacrylic acid was allowed to react with ϵ -caprolactone in molar ratio of 1/2.0 to obtain FM200A for Comparative Example.

Results are shown in Table X-1.

	lactone-added numbers	0	1	2	3	4	Total	average-added numbers	Mn
before removal of AA	FA050A	35.1	39.5	19	5.2	1.1	99.9	0.98	183
after removal of AA		0.0	61.0	29.3	8.0	1.7	100.0	1.50	244
before removal of AA	FA075A	23.4	36.4	25.8	10.5	3.9	100.0	1.35	226
after removal of AA		0	47.5	33.7	13.7	5.1	100.0	1.76	273
before removal of AA	FA200A	16.3	32.2	28.9	14.8	7.6	99.8	1.65	260
after removal of AA		0	38.6	34.6	17.7	9.1	100.0	1.97	297

	lactone-added numbers	0	1	2	3	4	Total	average-added numbers	Mn
before removal of MAA	FM050A	38.2	38.3	17.7	4.8	1	100.0	0.92	191
after removal of MAA		0	62.0	28.6	7.8	1.6	100.0	1.49	256
before removal of MAA	FM075A	23.4	36.4	25.8	10.5	3.9	100.0	1.35	240
after removal of MAA		0	47.5	33.7	13.7	5.1	100.0	1.76	287
before removal of MAA	FM200A	16.3	32.2	28.9	14.8	7.6	99.8	1.65	274
after removal of MAA		0	38.6	34.6	17.7	9.1	100.0	1.97	311

Application Example

A four-necked flask equipped with a thermometer, a reflux condenser, a tube for introducing nitrogen gas, and an agitator was charged with 50 parts of butyl acetate, 50 parts of toluene, and 1.0 part of ditertiarybutyl peroxide (DTBPO), followed by elevating a temperature to 115°C. At a period having attained to 115°C, there were added dropwise over 3 hours 17.3 parts of styrene, 17.3 parts of butyl methacrylate, 17.3 parts of butyl acrylate, 2.0 parts of methacrylic acid, 46 parts of the caprolactone-modified methacrylate composition synthesized in the Example 5, 0 part of 2-hydroxyethylmethacrylate, and 1.0 part of azobisisobutyronitrile, and a reaction was further continued for 4 hours to obtain an excellent transparent acrylic polyol resin solution.

In the case of employing a coating having a low proportion of the adducts in which not less than 2 mol of ϵ -caprolactone is added as, for example, a top-coating material for cars, there can be obtained a coating layer which is well-balanced among a hardness of a coating

layer, a finishing outer appearance, weatherability, acid resistance, stain resistance, gloss, flexibility, and abrasion resistance.

Possibility of utilization in Industry

According to the present inventions No.I to No.VII, there can be obtained a hydroxyalkyl(meth)acrylate composition modified by a small amount of lactones, an acrylic polyol resin (A) obtained by allowing to react the composition with other ethylenic unsaturated monomer, and a curable resin composition containing the resin can be employed as a raw material for, for example, a well-balanced high quality finishing agent for industry, for example, a coating, a pressure sensitive adhesive, an ultraviolet ray- and electron beam-curable coating agent, and a reactive improver, etc. by formulating various conventional crosslinking agents and usually employed components.

A composition containing the curable resin composition is excellent in workability, water resistance of a coating layer, acid rain resistance, staining resistance, retort resistance, adhesion, a low temperature curability, and wet ink adaptability and, by which there can be prepared a coating well-balanced between abrasion resistance and acid resistance, which is excellent in flexural resistance and recoat adhesion, and which can be employed as a raw material for coatings for cars, home electric appliances, a water-based coating for coating an outside and inside of cans for foods and beverages, particularly, a clear coating for finishing an outside of the cans, and a top coating for cars.

In a conventional type coating composition using a layer-formable resin, even in the case of employing a melamine resin curing agent

causing a worse acid resistance, there is produced a large merit that any problems are not caused by the use of a coating of the present invention.

The carboxylic group-contained acrylate monomer composition modified by a small amount of lactones in the present inventions No. VII to No. VIII has (meth)acryloyl group and carboxylic group in the molecule, and it has an effect in adhesion to a metal and other materials, solubility to water and an aqueous alkali solution and, above-all, reduction of a developing time of period in an alkali developing step for forming a pattern utilizing ultraviolet ray curing, and an improvement in removal property of an uncured portion. Further, the compound of the present invention can be industrially prepared at economical cost by an applicable method for the preparation thereof.

From the curable resin composition prepared by polymerization of the carboxylic group-contained acrylate monomer composition modified by a small amount of lactones, a high solid coating can be prepared, and a coating layer obtained from the coating is excellent in acid resistance against acidic rain, abrasion resistance, yellowing resistance, and outer appearance, and the coating can be cured at low temperature.

The polyester unsaturated monomer modified by a small amount of lactones of the present invention No. X can be readily prepared by an industrial fashion in a short step.

Since the polyester unsaturated monomer modified by a small amount of lactones obtained has one radically polymerizable unsaturated group, and it has carboxylic group at terminal, there can be widely expected an application as a raw material or an intermediate for a thermosetting coating, an adhesive, a crosslinking agent, a stabilizer for an emulsion, a dispersant, and an emulsifier, etc.

Further, in a composition using the polyester unsaturated monomer modified by a small amount of lactones, since tackiness can be removed by elevating Tg of the composition, it is particularly useful in an electric material field, etc.

Still further, there can be obtained the polyester unsaturated monomer modified by a small amount of lactones in which discoloration is low.

According to the present invention, there can be prepared a polyester unsaturated monomer modified by a small amount of lactones in which the amount of the lactones added is not less than 0.3 and more than 1 mol, and which has an identical radical polymerizable functional group to the number of a radical polymerizable functional group existing in a radically polymerizable unsaturated monomer having carboxylic group which is employed as a raw material. Particularly, in the case that acrylic acid and methacrylic acid are employed as the radically polymerizable unsaturated monomer having carboxylic group, there can be produced a polyester unsaturated monomer modified by a small amount of lactones which certainly has one piece of a radically polymerizable functional group without producing a compound not containing the radically polymerizable functional groups at all and a compound having two or more pieces of the radically polymerizable functional groups.

The polyester unsaturated monomer modified by a small amount of lactones obtained is characterized in that it has reactive carboxylic group at one terminal and, further, it has a radically polymerizable unsaturated group apart from the carboxylic group.